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THE

PHYSICAL REVIEW.

SOME CHARACTERISTIC CURVES FOR GASES AT LOW PRESSURES.

By Robt. F. Earhart.

A LARGE amount of data on the potential required to produce and to maintain a discharge through gases under varying conditions of pressure has been published by numerous observers. The data upon the value of the current strength of the discharge and the effect of varying potential, pressure and spark length upon the magnitude of the current are more limited.

Townsend in his book on Ionization by Collision has gathered much of the available data on the relation between potential gradient and current. The data there presented and discussed apply to a different phase of discharge than the one described in this article. Townsend discusses the currents produced in a gas by the action of some agent like X-rays or ultraviolet light. The sweeping of the ions thus formed out of the ionized region constitutes the current, the current values produced in most cases lying far below the saturation value.

The term characteristic curve used here is similar to the technical term as applied to a dynamo or similar electrical device and merely shows in a graphic way the relation between current and potential under a stated condition.

The problem as it appeared to the author at the inception of the experiments resolved itself into several questions of a rather simple character. Given a luminous discharge at low pressure between two electrodes: what effect will changing the potential produce? To what extent will a characteristic curve be modified by altering the gas pressure and the distance between the electrodes? What effect will altering the size of the cathode have on the characteristic curve? To what extent will these be modified if a diaphragm with orifices of different sizes be placed in different parts of the discharge path? What, quantitatively,

will be the effect of a constriction in the path of the discharge? So far as the author is aware the term characteristic curve used in the sense previously stated was first applied to gases by Kauffman.[1] The discussion is theoretical for the most part and the experimental data very limited. In 1901 Rieche[2] studied the relation between potential and current in gases under low pressures, but considered particularly the effect of a magnetic field on the characteristic curves. Both Warburg and Tamm have made experiments on the relation between current and potential for pressures of the order of atmospheric pressures and have stated their results in empirical formulæ. It may well be doubted whether their formulæ could be extrapolated to pressures of the kind used in a Geissler tube. In fact the observations recorded in this paper indicate that much larger currents are obtained at lower potentials as the pressure approaches the critical value, than would be anticipated from their formulæ. A digest of the experiments by Warburg and by Tamm is given by Sir J. J. Thomson in his Conduction of Electricity through Gases, pages 501–502. Two articles by Zeleny[3] constitute a comprehensive extension of the subject. His account of the variation of current and potential for the lower pressures is very brief. Mention is made of the fact that between pressures of 1 and .01 cm. large variations of current are produced with small changes in potential. The present article is concerned with pressures lying wholly within such limits. In a paper recently published by the author,[4] it appears that currents of considerable magnitude may be secured if the cathode is of generous dimensions. The apparatus used in this experiment is fully described in the previous article and will be but briefly mentioned here. A plate made up of ten concentric brass rings separated by an insulating material served as a cathode. The face of the cathode was in a horizontal plane and had a total conducting area of 85 sq. cm. The anode consisted of a hemisphere of Pt (of 1 mm. radius), mounted on a vertical brass rod. The brass rod was covered with a thin glass envelope leaving only the hemisphere exposed. The anode was capable of adjustment vertically and was always symmetrical with reference to the cathode. The discharge apparatus was contained in a bell jar of approximately 10 liters capacity. Measurement of the current which passed through any or all of the rings which together make up the cathode could be made. In the present case the rings were usually connected in parallel. The potential difference between the

[1] Gottingen Nach., 1899, p. 243.

[2] Annal. d. Phys., 1901, 4, p. 292.

[3] J. Zeleny, PHYS. REV., 25, p. 305, 1907; 26, p. 129, 1908.

[4] PHYS. REV., Mar., 1912, p. 188.

electrodes was produced by 450 storage cells and regulated by means of a cadmium-iodide-amyl-alcohol resistance. Potential was determined by means of a Weston voltmeter with multiplier in series and current measured directly with a Siemans and Halske milliammeter. The experiments may be grouped under four heads and will be taken up in that manner.

I. The characteristic curves between the sphere and plane for different pressures and for distances ranging from 1 to 4 centimeters.

II. Effect of changing the area of the cathode on the characteristic curves.

III. Effect of the introduction of thin diaphragms with apertures of different dimensions in the path of the discharge.

IV. Effect of a constriction. Length of constriction. Size of constricted portion. Location of the constricted portion.

I. Effect of Distance and Pressure upon the Characteristic Curves.

The cases studied experimentally in this connection were taken with the full cathode plate, 85 sq. cm., and with the anode at distances of 1 cm., 2 cm., 3 cm. and 4 cm. under various conditions of pressure. These are represented graphically in Figs. 1 to 12. In Figs. 1–4 the results obtained for air are given and in a general way are typical. Figs. 5 to 8 are for hydrogen and Figs. 9 to 12 for carbon dioxide. The form of the characteristic curve is the same for each gas. For hydrogen lower potentials than those necessary for air sufficed, while higher potentials were required for carbon dioxide. The apparatus as constructed made it possible to study the distribution of current density over the cathode. This was done in some cases, but has been discussed in a previous paper. The usual method of procedure was as follows: A discharge was produced, usually by making the sphere negative and then reversing the polarity of the electrodes, the current was raised to the maximum value and allowed to run for 10 or 20 minutes. The current was then reduced by increasing the resistance in the circuit by small steps. Frequent measurements were made upon the potential and current. These are represented in the graph. Many measurements were made at other pressures but are not incorporated in the figures. It may be noticed that for the lower pressures two current values are possible for the same potential, but the distribution over the plate differs in the two cases. When the current has the least value, the resistance in the circuit is a maximum and the potential difference between the electrodes exceeds the minimum value. The discharge is then confined to a limited portion of the cathode.

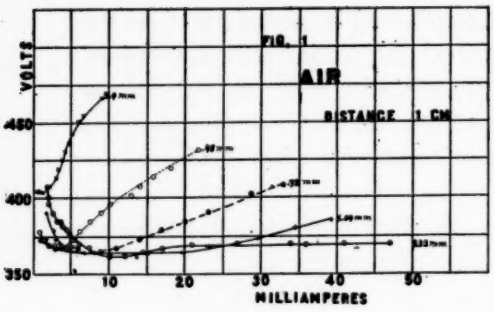
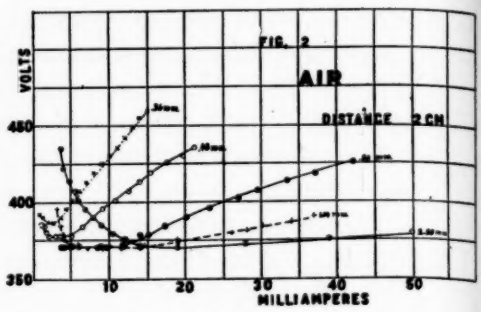


Fig. 1.



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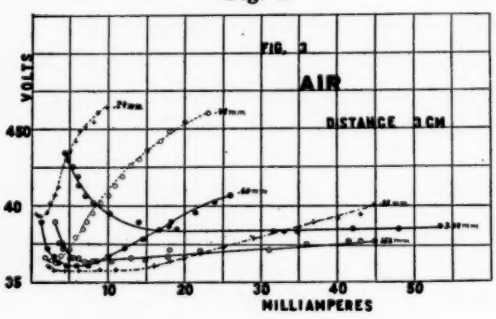
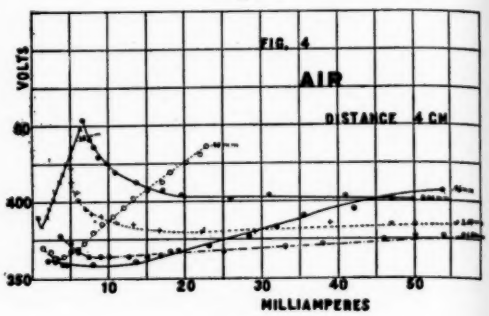


Fig. 3.



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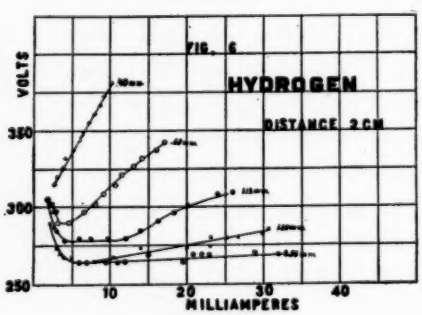
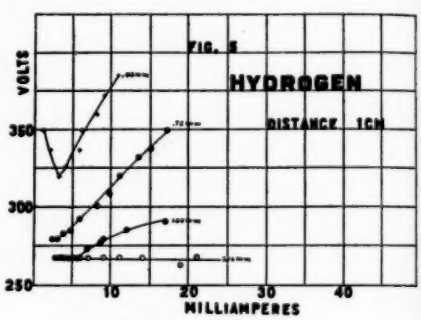


Fig. 5.



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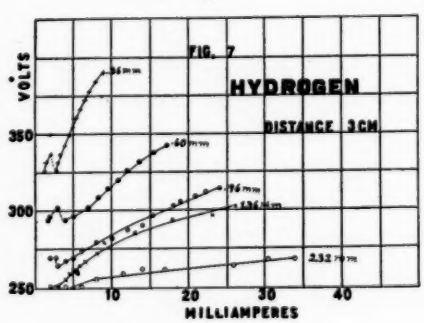


Fig. 7.

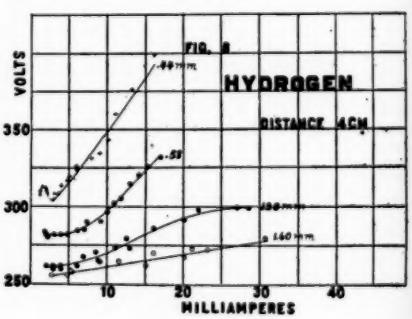


Fig. 8.

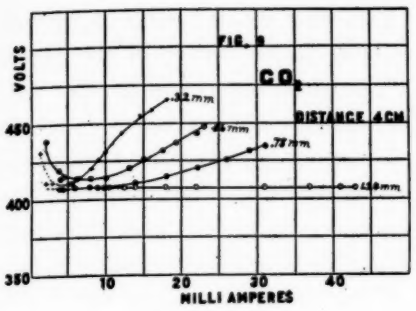


Fig. 9.

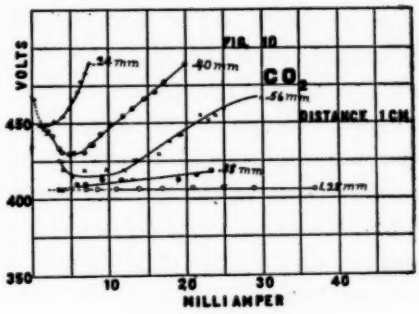


Fig. 10.

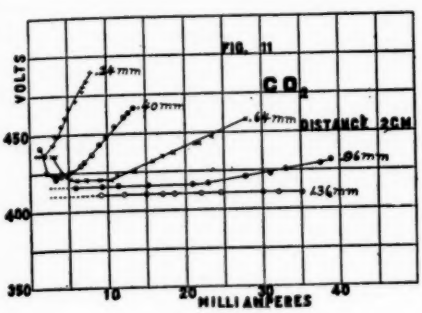


Fig. 11.

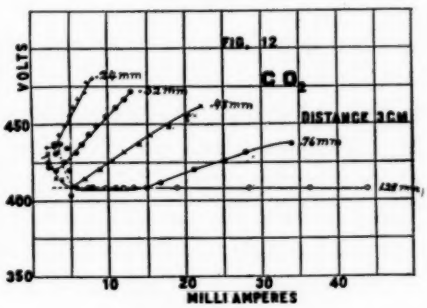


Fig. 12.

Should the pressure be above the critical value the discharge will be confined to the inner zones; should the pressure lie below the critical value, to the outer zones. When the resistance of the circuit is decreased the potential falls, the current increases and the luminosity spreads out over the plate. After the entire plate is functioning, decreasing the resistance causes a rise in current accompanied by a rise in potential between the electrodes. The increase in current density after this stage is reached is not uniform over the plate, but is greatest over the outer zone. It may be noticed that for the higher pressures, the largest currents obtained do not require a potential exceeding the minimum value. It was observed in such cases that the minimum discharge occurred between the inner zones and the anode and as the current increased the discharge spread over the cathode but never reached the edges of the plate. Near the critical pressure, as the current was diminished and the luminosity ceased to cover the cathode an unstable condition existed in which the luminous patch moved about over the plate. In general, while the redistribution takes place there is an unstable condition and the branch of the curves representing the smaller values of the current has a region of instability. This is particularly true for hydrogen which presented an anomaly. In obtaining the hydrogen curve the current

was decreased in the usual manner. This was accompanied by rise in potential when the discharge drew in toward the center of the plate. At a certain stage, as the current was decreased the potential also fell, passing through an unstable region, but with further decrease in current the potential rose in a perfectly normal manner. This gives rise to the peculiar kink in the hydrogen curve in this region. Modification of the current control, by altering the batteries and control resistance indicated that it was not an error due to some peculiarity of manipulation but occurred each time under the same condition of pressure and potential. No explanation of this is vouchsafed. The hydrogen was prepared in a Kipp apparatus by the use of C.P. acid on aluminium turnings and was purified and dried. No similar kink was found for either air or carbon dioxide.

Before leaving this phase of the subject it may be of interest to indicate the extent to which the condition of the cathode surface influences the characteristic curve. In the experiments just described, care had been taken to have the cathode smooth, free from scratches and clean. The smooth cathode was covered with a handful of brass turnings and filings. These were spread out in such a manner as not to decrease materially the distance between the electrodes but served to give a rough surface. The characteristic curve was modified but slightly. The apparent effect was to increase the range of instability. The roughening of the plate had in general no effect on the form of the characteristic curve or on the numerical values which relate potential and current. The empirical formulæ based on measurements for high pressures and which connect pressure, potential, and current for a positively electrified point when extrapolated into this region, give values much smaller than those observed. No attempt has been made to develop a new relation for the variations in the region, for it will be seen later that these are further complicated by the size of the cathode.

II. Effect of Size of Cathode on the Characteristic Curves.

Figs. 13 to 16 show the relation between current and potential when the distance between the anode and central part of the cathode was 4 cm. and air used as the dielectric. The characteristic curves shown are for pressures ranging from those less than to those greater than the critical pressure for this distance.

As noted previously, as soon as the cathode is completely covered with the luminosity and is functioning over the entire available area, there will be a rise in potential with increase of current. With the smaller cathode this condition will be attained for smaller values of current

than with the larger cathode. The numerals accompanying the various curves refer to the cases given in the accompanying table.

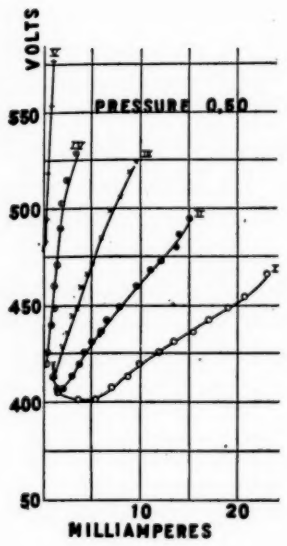
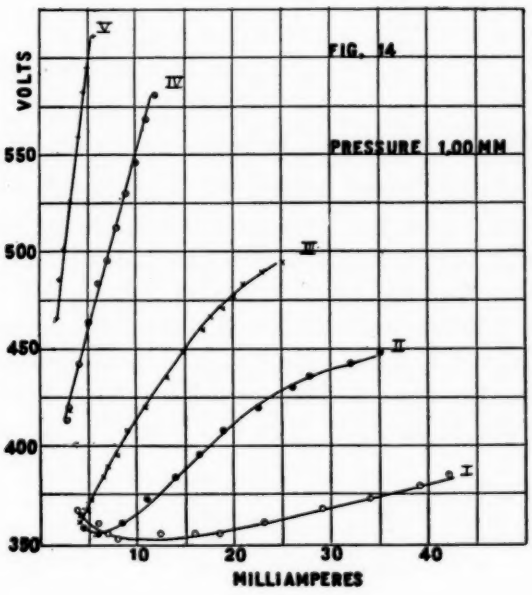


Fig. 13.



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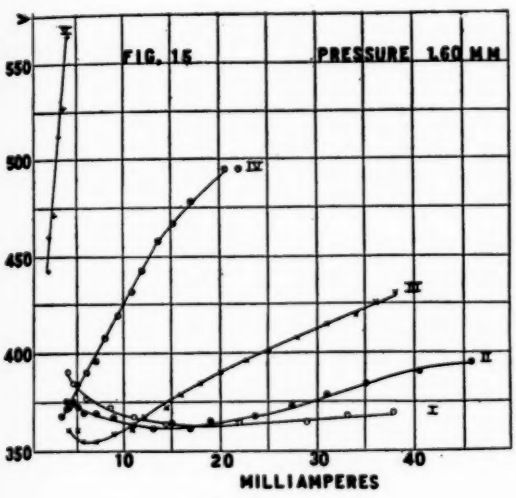

Fig. 15.

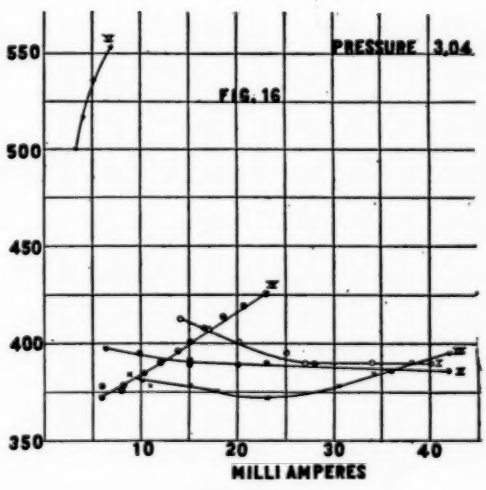

Fig. 16.

The area of the different plates is given. If a line be drawn from the midpoint of the cathode plate to the anode and another from the edge of the plate to the anode these lines will include the angle α.

Case.	α	Area of Cathode in Sq. Cm.
I.	54° 42′	85.0
II.	43° 54′	39.8
III.	33° 25′	19.0
IV.	12° 00′	5.9
V.	3° 36′	.2

III. Effect of Diaphragms in the Path of the Discharge.

The full-sized cathode was used in this experiment. The anode was four centimeters from the plane of the cathode and placed symmetrically with reference to it. The outer zone of the cathode was surrounded by a ring of fiber. Over the top of this spacing ring a very thin diaphragm of mica was sealed. The part directly underneath the anode was pierced. Orifices of 5 mm., 2 mm. and 1 mm. diameter were used. By means of spacing rings of different heights these diaphragms were placed successively at distances of .5, 1, 2, 3, and 3.5 cm. above the cathode. Char-

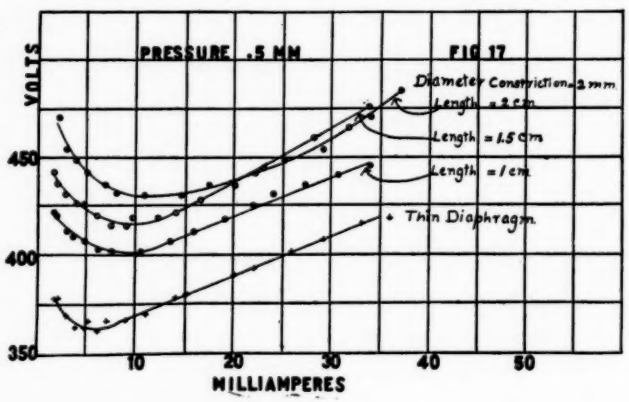

Fig. 17.

acteristic curves were taken for three pressures in each case; fifteen cases in all, making forty-five characteristic curves. The differences obtained between any of these and the curves secured when no obstruction was present, was so slight that it may be asserted that the introduction of the diaphragms had no effect on the characteristic curve. Their introduction however increased the stability of the discharge. The appearance of the discharge is also modified. In addition to the luminosity over the cathode and at the anode there is a luminous patch in the aperture. The intensity of the luminous patch is much greater for the small openings. The characteristic curve for the 2 mm. opening is the lowest one in Figs. 17, 18 and 19, and differs very little from the corre-

sponding curves in Fig. 4, which shows the case when no diaphragm is interposed. It is well known that the potential gradient along a discharge of this character is not uniform but that the rate of change of

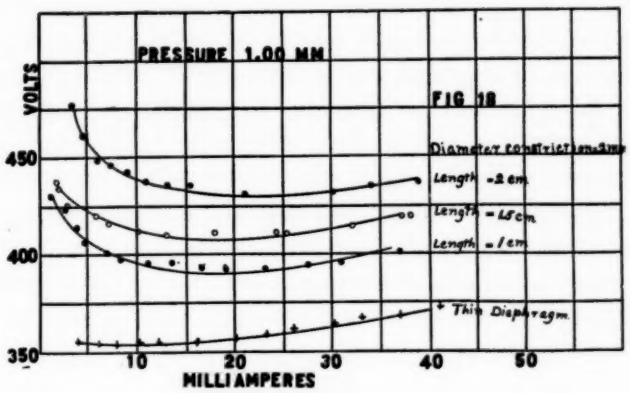

Fig. 18.

potential is greater near the electrodes, especially at the cathode. The diaphragms in all cases were interposed where the electric force is weak. It thus appears that the convergence of the stream lines for a short distance has little appreciable effect on the total potential fall.

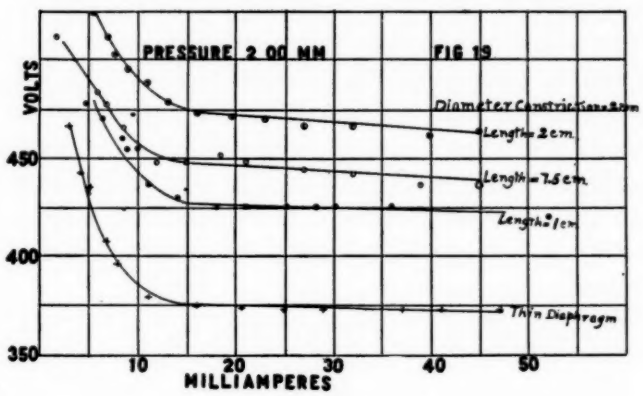

Fig. 19.

IV. Effect of a Constriction in the Path.

The modification of the apparatus for this portion of the experiment consisted merely in piercing a diaphragm and inserting glass tubes of different lengths and bores. The constriction tubes were placed directly underneath the anode and symmetrical with reference to the cathode unless otherwise stated.

The tube was sealed into the mica diaphragm with waterglass and all the discharge passed through the tube. By means of spacing rings this was placed in turn at different elevations above the cathode. The lower end was placed 2 mm. above the cathode, again with the upper end of the tube 2 mm. below the anode and in the midposition. The effect of the introduction of the tube was considerable, but the location of the tube so far as elevation was concerned introduced no further variation, at least within the limits mentioned. The fiber spacing ring which with the mica diaphragm served to enclose the cathode was removed and a glass ring substituted. This permitted an unobstructed view of the entire phenomena occurring within the apparatus. The diameter of the constriction tubes employed ranged from 5 mm. to 1.85 mm. Figs. 17, 18 and 19 show the effect of introducing constrictions of different lengths. They indicate that the increase in potential necessary to maintain a given discharge through the constriction increased directly as the length of the constricted portion. The tube employed in securing the data shown by the curve was 2 mm. in diameter. The characteristic curves in each case are displaced upward with increasing length of tube, indicating that the increase in potential required to maintain a given current through the constriction over that for the unobstructed discharge is similar to the increase of a wire with length. If the increase in the apparent resistance is due to the crowding together of the stream-lines then confining these to increasing lengths will cause an increase in the resistance varying directly as the lengths of the constricted portions. In Fig. 17, where the pressure used was .5 mm., the curve for the discharge through the longest tube cuts across the one representing the one of less length. This is due, in my opinion, to the fact that in this region small variations of pressure produce relatively large changes in current density. A very slight error in reading the pressure would account for this.

Varying the area of the constricted portion produced smaller changes than variations of length. Variations of area in the ratio of 10 to 1 produced relatively small variation as compared with the effect of varying the lengths. Tubes whose diameters were smaller and others larger were varied in length and gave results in agreement with those represented for the 2 mm. tube. The larger tubes had the corresponding characteristic curves shifted upward less than the smaller tubes but the shift was not proportional to the inverse ratio of the areas.

In the case of tubes of small bore it is difficult to start a discharge through them. For the smallest tubes employed there is a very limited range of pressure and potential for which a discharge may be induced to

start. Once established, the pressure and potential could be changed through rather wide limits. The range of potentials at my disposal limited the experiments to tubes of about 1.5 mm. diameter if tubes longer than 1 cm. were to be employed, hence these observations were not extended to tubes of smaller bore.

A series of measurements was made with a tube of 2 mm. bore and 15 mm. length, the constriction being set our laterally. The constriction tube was first set out 1.5 cm. from the center of symmetry. The shift in the characteristic curves which resulted for this offset was inappreciable for the lower pressures, .5 mm. and 1 mm., but for the highest pressure, 2 mm., the curve was shifted upward, indicating an increase in the apparent resistance. When the same tube was set out 3 cm. from the line of symmetry the characteristic curves for the two larger pressures were shifted. Finally when the offset was 4.5 cm. all of the curves were displaced; the one corresponding to the highest pressure to a much greater extent than the others.

SUMMARY.

I. Characteristic curves for air, hydrogen and carbon dioxide in the region of the critical potentials have been obtained.

II. The strength of the current through a gas at low pressures is determined in part by the size of the cathode. Empirical formulæ for the discharge from a positively electrified point cannot be extrapolated from high pressure and potential regions to low pressure conditions.

III. Introducing a constriction into the path of a discharge has the effect of increasing the apparent resistance of the circuit. The increase in the apparent resistance varies directly with the length of the constricted portion.

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OHIO STATE UNIVERSITY,
May 26, 1912.

VISCOSITY AND FLUIDITY—A SUMMARY OF RESULTS.[1] II.

EUGENE C. BINGHAM.

FLUIDITY AND OTHER PHYSICAL PROPERTIES.

Fluidity and the Boiling-Point.—Thorpe and Rodger[2] have measured the viscosities of a very large number of liquids and with great care from 0° to nearly the boiling-point of each liquid. The corresponding fluidities have been calculated by Miss Harrison and the writer. When a line is drawn through the fluidities of a given class at the boiling temperatures as extrapolated, the resulting curve in a surprising number of cases turns out to be a straight line, as shown in Figs. 12–16. In those classes of

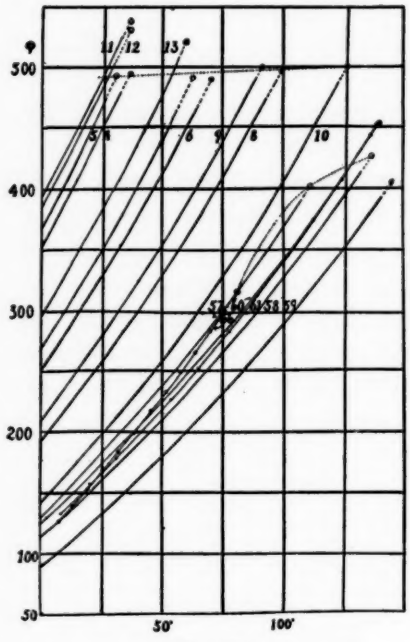


Fig. 12.

The fluidities of various hydrocarbons at different temperatures. 4, pentane; 5, isopentane; 6, hexane; 7, isohexane; 8, heptane; 10, octane; 11, trimethylethylene; 12, isoprene; 13, diallyl; 56, benzene; 57, toluene; 58, ethylbenzene; 59, (*o*)-xylene; 60, (*m*)-xylene; 61, (*p*)-xylene.

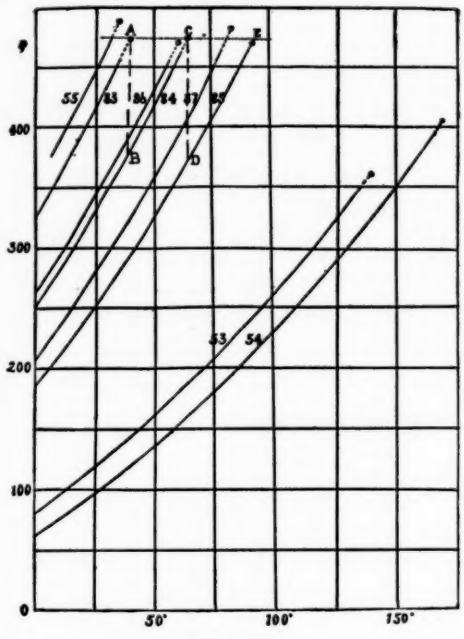


Fig. 13.

The fluidities of various ethers and acid anhydrides at different temperatures. 53, acetic anhydride; 54, propionic anhydride; 55, diethyl ether; 83, methylpropyl ether; 84, ethylpropyl ether; 85, dipropyl ether; 86, methylisobutyl ether; 87, ethylisobutyl ether.

[1] For Part I., see the PHYSICAL REVIEW, December, 1912.

[2] Phil. Trans. (London), *185A*, 397 (1894); *Do.*, *189A*, 71 (1897).

compounds which are usually regarded as associated, as the aromatic hydrocarbons, acids, alcohols, esters, and ketones, the fluidities of a

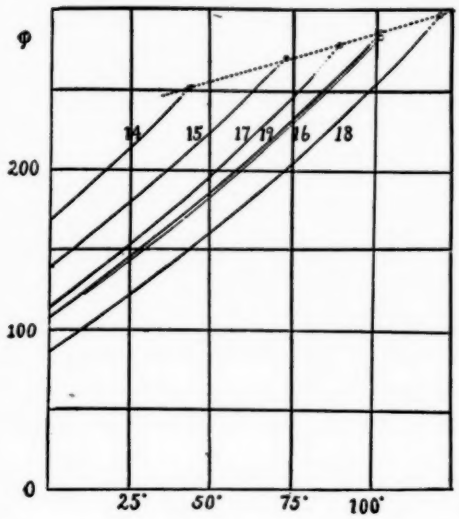


Fig. 14.

The fluidities of various alkyl iodides at different temperatures. 14, methyl iodide; 15, ethyl iodide; 16, propyl iodide; 17, isopropyl iodide; 18, isobutyl iodide; 19, allyl iodide.

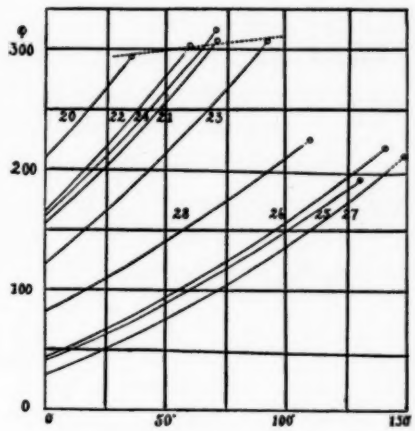


Fig. 15.

The fluidities of various bromine derivatives of the hydrocarbons at different temperatures. 20, ethyl bromide; 21, propyl bromide; [22, isopropyl bromide; 23, isobutyl bromide; 24, allyl bromide; 25, ethylene bromide; 26, propylene bromide; 27, isobutylene bromide; 28, acetylene bromide.

homologous series at the boiling-point still fall on a smooth curve, but this curve is no longer a straight line, as seen in Figs. 12, 16 and 17.

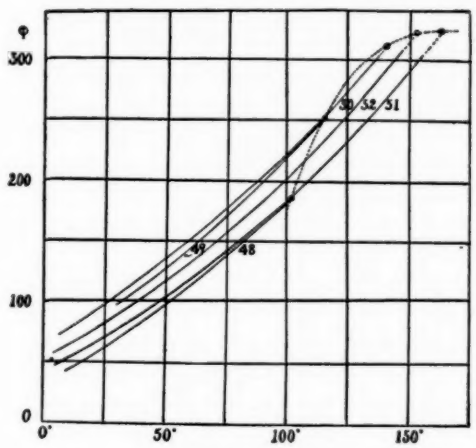


Fig. 16.

The fluidities of various organic acids at different temperatures. 48, formic acid; 49, acetic acid; 50, propionic acid; 51, butyric acid; 52, isobutyric acid.

It is quite improbable that these relationships are due only to accident. They have remained undiscovered for the most part, because of the hyperbolic nature of the viscosity curves and because the viscosities at the boiling-points are very small, making the relation uncertain. Finally the linear fluidity-boiling-point curves of the unassociated classes would themselves be hyperbolas when changed on to the viscosity basis, thus adding to the complication.

The effect of adding a methylene group to any compound is to raise the boiling-point and to lower the fluidity. The meaning of the relation which we have noted seems to be that the ratio between these effects is constant, or in Fig. 13 $AB/AC = CD/CE$.

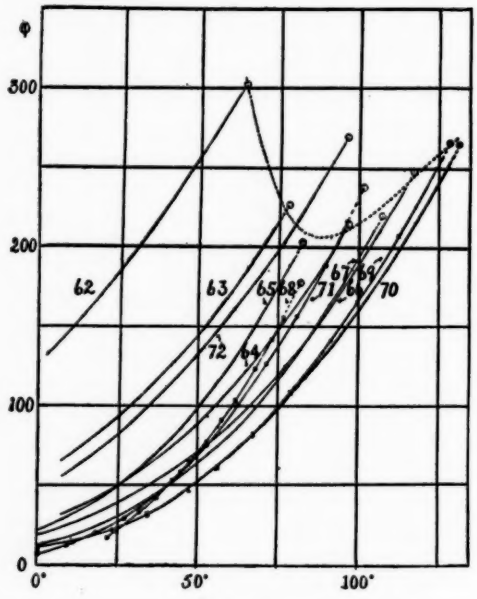


Fig. 17.

The fluidities of various alcohols at different temperatures. 62, methyl alcohol; 63, ethyl alcohol; 64, propyl alcohol; 65, isopropyl alcohol; 66, butyl alcohol; 67, isobutyl alcohol; 68, trimethylcarbinol; 69, active amyl alcohol; 70, inactive amyl alcohol; 71, dimethylethylcarbinol; 72, allyl alcohol.

Fluidity and Vapor Pressure.[1]—It is better perhaps to regard it merely as a coincidence that for the classes of aliphatic hydrocarbons and ethers the fluidity of every member of the class at its boiling-point is nearly identical. But it is quite unlikely that this coincidence is peculiar to the vapor-pressure of 760 mm., therefore it is desirable that it be shown that this relation holds for all vapor-pressures. If it be true for a given

[1] Cp. ninth and thirteenth papers.

class that, at any given vapor-pressure, the fluidities are identical, it follows that the vapor-pressure-fluidity curves of the whole class should fall together into a single curve, for the fluidities of all of the different members of the class at any given vapor-pressure would form but a single point of the curve. How far this is the case is shown in Fig. 18 for the

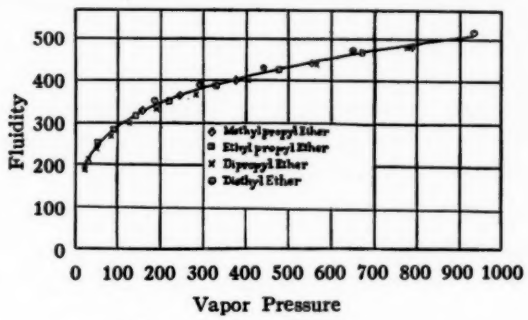


Fig. 18.

Fluidity-vapor-pressure curve of ethers.

class of ethers so far as the requisite data have been obtained. The fluidities were measured by Thorpe and Rodger, the vapor-pressures were measured by the author by the method of Ramsay and Young.[1] A similar relation is found to hold for the aliphatic hydrocarbons.

This relation does not hold true for the other classes, but it has been pointed out that the other classes of unassociated substances also have linear boiling-point-fluidity curves and that it may be regarded as a coincidence that the fluidity of the classes of ethers and hydrocarbons are identical; hence it seemed desirable that a method be worked out for comparing the fluidity-vapor-pressure curves of these other classes.

The fluidity-vapor-pressure curves of all unassociated compounds are similar but not coincident. The fluidity of the aliphatic hydrocarbons at their boiling points is around 500 cm.g.$^{-1}$ sec. units. Taking the round number 500 as the standard, all other fluidities may be reduced to those of a substance which has a fluidity of 500 at the boiling-point—the general properties of the curve remain the same as before. Thus heptane has a fluidity at the boiling-point (98.4° C.) of 503.9. At 90° C. heptane has a fluidity of 468.3 absolute units and a vapor-pressure of 588.8 mm.

[1] Professor Alexander Smith has kindly called my attention to the omission in my paper of the correction for the depression of the mercury in the thermometer due to the expansion of the glass under the diminished pressure. Probably the error in this case was relatively small because the pressures were not very low, but it should not have been neglected.

I may here call attention to a correction in my twelfth paper, Am. Chem. J., *46* (1911). On page 288, column three of Table XII. should read, "Volume per cent. of clay 1.015, 1.009, 1.003, 0.991, 0.977, 2.570, 2.565, 2.552, 2.542, 2.531, 4.603, 8.390."

Reducing this fluidity to standard we have $468.3 \times 500 \div 503.9 = 464.7$. By plotting the curves of a large number of substances we could obtain a composite curve which might then be regarded as the standard curve. There are obvious reasons, however, for choosing the curve of a known substance as the standard curve for reference, hence we have chosen heptane, since its fluidities and vapor-pressures are known over a considerable range and its fluidity-vapor-pressure curve is close to the composite curve.

We have elsewhere[1] given a table of vapor-pressures corresponding to the various fluidities of heptane, reduced as indicated above. By comparing the observed vapor-pressures of any substance with the values calculated by the use of this table, one can prove that the relation between fluidity and vapor-pressure in the different classes of substances is quite general, the highly associated substances alone being exceptional. The agreement is shown for a single substance, methyl isobutyrate, in the following table. The fluidity at the boiling-point (92.3°) is 397.3.

TABLE I.

The Vapor-Pressures (p) of Methyl Isobutyrate Calculated from Its Fluidities Reduced to 500 C.G.S. Units at the Boiling Point.

Temp.	ϕ Red.	p Obs. in Cm.	p Calc. in Cm.	Per Cent. Diff.	Temp.	ϕ Red.	p Obs. in Cm.	p Calc. in Cm.	Per Cent. Diff.
0	187.3	1.22	1.02	−17	50	338.3	16.20	16.20	0
10	214.7	2.24	1.98	−12	60	372.8	24.38	24.44	0
20	243.3	3.89	3.55	− 6	70	409.6	35.53	35.93	1
30	273.0	6.54	6.17	− 6	80	449.2	50.50	51.76	2
40	304.7	10.47	10.29	− 2	90	490.9	70.70	71.60	1

There is general agreement when the vapor-pressures are not too small and the compound not highly associated. From a study of a considerable number of compounds, we have found that for vapor pressures of more than ten centimeters, the calculated values differ from the observed by only a little over three per cent.

Since this relation exists, it is possible to calculate unknown vapor-pressures of unassociated compounds, when the boiling-point of the compound is known. Conversely, if the vapor-pressures of a substance and its fluidity at the boiling point are known, it becomes possible to construct the fluidity curve. Thus suppose that the fluidity of ethyl-propyl ether at 20° C. is desired, it being known that the fluidity of this substance at the ordinary boiling-point is 479.9 and that its vapor-pressure at 20° is 14.26 cm. The corresponding fluidity interpolated

[1] Am. Chem. J., 47, 187 (1912).

from the table for heptane, the standard substance, is 328.0; but these fluidities are reduced, so that they must be corrected back. Thus $328.0 \times 479.9 \div 500 = 314.8$, which is practically identical with the observed value of 314.9.

A priori, one would hardly expect to find any relation at all existing between the fluidity of a liquid and the pressure of the vapor above it. Yet it is proved that a relation does exist of a very simple character. This is doubtless the result of both of these properties being similarly dependent upon another property of the liquid, which is probably its molecular volume.

As has been already hinted, the calculated values of the vapor-pressure differ very widely from the observed values in the case of highly associated liquids. A discussion of these interesting cases would carry us beyond the limits of this paper.

Finally it is important to point out that the above relation could hardly have been discovered on the assumption that viscosities are additive. The viscosity-vapor-pressure curves must be hyperbolic in character, although like the viscosity curves some of them might appear to be linear, as would indeed those of the ethers and aliphatic hydrocarbons.

Fluidity and Chemical Composition and Constitution.[1]—As soon as any considerable amount of viscosity data had been collected, it became evident to the early workers in this field that there is a relation between viscosity and chemical composition. At the hands of Pribram and Handl[2] the number of empirical relations became quite extended, although their experimental material lacked great precision. This seemed to Thorpe and Rodger to indicate that results of great importance might be obtained if very accurate data were available for a sufficient variety of substances of unquestioned purity. Consequently these investigators began the accumulation of viscosity data considering carefully every detail of the purification of material, precision in measurement, and accuracy in the calculation of results. Their monumental work[3] finally embraced some 85 substances. To bring out new relationships, it became necessary to find the proper basis of comparison. For this purpose Thorpe and Rodger studied their data from every point of view which occurred to them. They compared viscosity coefficients, molecular viscosities, and molecular viscosity work, at the boiling-point, critical temperatures, temperatures corresponding to a given slope of the viscosity curves, and viscosities corresponding to a given slope of the viscosity

[1] Cp. sixth paper.

[2] Sitzungsber. der math.-naturwiss. Klasse der Kais. Akad. d. Wiss. Wien, *78*, II., 113 (1878); *Do.*, *80*, II., 17 (1879); *Do.*, *84*, II. 717, (1881).

[3] *Loc. cit.*

curves. They confirmed the conclusion that different atoms and groupings have, in general, an additive effect upon the viscosity, but as a whole their results are disappointing, for the value of an atom or grouping is sometimes arbitrarily assumed to vary from class to class. Thus oxygen has one value for ethers, another for alcohols, and still another for acids. But even with these assumptions, a considerable number of substances fail to give satisfactory results upon any basis of comparison. They obtained best results in comparisons at equal slope, although their argument to prove that this should be the case is scarcely conclusive.

If the fluidities are additive, and not viscosities, it seems probable that the true basis of comparison should be worked out in comparing fluidities and not viscosities as has been done uniformly heretofore. Inspection of Figs. 12–16 shows that in homologous series, the fluidity-temperature curves form a family of approximately straight and parallel lines. Were they actually linear and parallel, their slopes and intercepts would of course completely define them, and give us therefore a true basis of comparison. Hence it seems certain that we should either compare fluidities at a given temperature or temperatures of equal fluidity together with the slopes of the fluidity curves. Since the curves in a given class are nearly parallel, it is evident that the slope is characteristic of the class to which a compound belongs. The molecular weights of the compounds determine the values of the intercepts. But the fluidity-temperature curves are neither perfectly linear nor parallel. The lack of linearity may be ascribed to association, using that term broadly. It should be recalled at this point that metallic mercury gives a fluidity curve which is quite linear and apparently cuts the temperature axis at absolute zero. It is probable that all fluidity curves would unite at absolute zero, so that exact parallelism is not to be expected even within a given class.

There are several reasons for comparing the temperatures of equal fluidity rather than fluidities at a given temperature.

1. The slopes are more nearly equal when the fluidities are the same.

2. At a given fluidity the members of at least two classes have the same vapor-pressure, and experience has proved that substances are comparable at temperatures corresponding to equal vapor-pressure.

3. The fluidity curves for associated compounds depart widely from linearity at low fluidities, but approach linearity at high fluidities, as do the curves of other compounds.

4. A yet more cogent reason grows out of the fact, mentioned above, that exact parallelism in the curves of a given class is not to be expected. A methylene group added to pentane, for example, lowers the fluidity a

certain amount, but a methylene group added to decane cannot lower the fluidity by the same amount, since as the molecular weight increases the fluidity must approach zero asymptotically. Otherwise, it would require no very high molecular weight to give a negative fluidity, which is inconceivable.

The fluidity of 200 was chosen for the basis of comparison since most substances could then be included. The temperatures and slopes of several unassociated compounds corresponding to the fluidity of 200 are given in Table II.

TABLE II.

Absolute Temperatures and Slopes of Non-Associated Substances Corresponding to a Fluidity of 200 C.G.S. Units.

Substance.	Abs. Temp. ($\phi = 200$) Observed.	Diff. CH_2.	Slope at ($\phi = 200$).	Abs. Temp. ($\phi = 200$) Calc.	Per Cent. Diff.
Hexane	(255.1)[1]	(21.0)	(2.88)	254.6	0.2
Heptane	276.1			277.3	0.4
Octane	299.1	23.0	2.44	300.0	0.3
Isohexane	(249.0)		(2.79)	247.0	0.8
Isoheptane	269.2	(20.2)	2.68	269.7	0.2
Methyl iodide	290.2		1.92	287.4	1.0
Ethyl iodide	309.2	19.0	1.80	310.1	0.3
Propyl iodide	332.7	23.5	1.82	332.8	0.0
Isopropyl iodide	324.5		1.92	325.2	0.2
Isobutyl iodide	345.5	21.0	1.86	347.9	0.7
Allyl iodide	330.5		1.82	328.8	0.5
Ethyl bromide	268.7		2.22	273.5	1.8
Propyl bromide	296.6	27.9	2.08	296.2	0.1
Isopropyl bromide	289.4		2.22	273.5	1.8
Isobutyl bromide	315.0	25.6	2.08	311.3	1.1
Ethyl propyl ether	(255.0)		(2.70)	256.1	0.5
Dipropyl ether	279.0	(24.0)	2.62	278.8	0.1
Methylissbutyl ether	(251.1)		(2.75)	248.5	1.0
Ethylisobutyl ether	270.1	(19.0)	2.68	271.2	0.4

TABLE III.

The Value of the Iso-Grouping.

Substance.	Temp. Obs. Normal Grouping.	Temp. Obs. Iso-grouping.	Diff.
Hexane	255.1	249.0	6.1
Heptane	276.1	269.2	6.9
Propyl iodide	332.7	324.5	8.2
Propyl bromide	296.6	289.4	7.2
Propyl chloride	261.5	255.2	6.3
Butyric acid	381.6	371.6	10.0
Methyl butyrate	304.2	295.8	8.4

[1] Values in parentheses are extrapolated.

Column 3 of Table II. shows that the value of a methylene group varies around a mean value of 22.7. The effect of an iso-grouping is to decrease the fluidity of a compound some 7.6 units, as shown in Table III.

The value of the hydrogen atom is calculated as follows:

TABLE IV.

The Value of the Hydrogen Atom.

Substance.	Temp. Obs.	$n \times CH_2$ Calc.	Diff.
Hexane	255.1	136.2	118.9
Heptane	276.1	158.9	117.2
Octane	299.1	181.6	117.5
Isohexane	249.0	128.6	120.4
Isoheptane	269.2	151.3	117.9

The mean value for H_2 is 118.4. Hydrogen has therefore a value of 59.2 and carbon of $-$ 95.7.

The value of the "double bond" in allyl compounds is obtained from Table V.

TABLE V.

The Value of a Double Bond.

Substance.	Temp. Obs. Normal Propyl.	Temp. Obs. Allyl.	Diff.
Iodide	332.7	330.5	2.2
Bromide	296.6	292.2	4.4
Chloride	261.5	256.0	5.5

To raise the fluidity of an allyl compound to 200 it is therefore only necessary to raise it to a temperature which is some four degrees lower than is required for the corresponding normal compound, containing two more hydrogen atoms. Thus the "double bond" has a value of 114.4, the absence of the hydrogen atoms being nearly compensated for by the "condition of unsaturation."

Assuming that the ethers are unassociated, we may obtain the value of the oxygen atom.

TABLE VI.

The Value of the Oxygen Atom.

Substance.	Temp. Obs.	C_nH_{2n+2}.	Oxygen.
Ethylpropyl ether	254.9	231.9	23.0
Dipropyl ether	279.0	254.6	24.4
Methylisobutyl ether	251.4	224.3	27.1
Ethylisobutyl ether	270.3	247.0	23.3

This gives an average value for oxygen of 24.2. The values of sulphur and the halogens are obtained similarly but need not to be given here.

From these values, the temperatures corresponding to a fluidity of 200 may be calculated. Some of these calculated values are given in the fifth column of Table II. A comparison between the observed and calculated values for 35 substances gives an average percentage difference of less than 0.8 per cent. The constants found at a fluidity of 300 are entirely consistent with these found at a fluidity of 200. The association is smaller at the higher temperatures as would be expected, and thus the temperature coefficients of association have been calculated,[1] but need not be given here.

In comparing viscosities, it has been customary to give an important special value to a ring grouping, but we have found that in comparing fluidities the value of the ring grouping is of small importance and may perhaps be neglected in a first approximation; for it would diminish the immediate usefulness of the method if a special value had to be assigned for each constitutive difference.

From the constants at different fluidities it is evidently possible to construct the entire fluidity curve of any unassociated substance.

Fluidity and Association.[2]—In the above calculations of constants it has been assumed that the compounds chosen are non-associated. This is probably not entirely warranted, but they must be associated to nearly the same extent since the agreement between the calculated and observed

TABLE VII.

Absolute Temperatures and Slopes of Some Associated Compounds Corresponding to a Fluidity of 200 C.G.S. Units.

Substance.	Abs. Temp. for ($\phi = 200$) Obs.	Abs. Temp. for ($\phi = 200$) Calc.	Slope for ($\phi = 200$).	Association.
Water	328.9	142.6	3.04	2.31
Formic acid	(380.2)	185.5	(2.18)	2.05
Acetic acid	363.8	208.2	2.06	1.77
Propionic acid	362.0	230.9	1.92	1.57
Butyric acid	381.6	253.6	1.92	1.57
Isobutyric acid	371.6	246.0	2.00	1.51
Methyl alcohol	305.2	165.3	2.78	1.84
Ethyl alcohol	343.4	188.0	3.24	1.83
Propyl alcohol	365.6	210.7	3.76	1.74
Butyl alcohol	377.0	233.4	3.44	1.62
Ethyl formate	273.8	230.7	2.40	1.19
Ethyl acetate	284.0	253.4	2.50	1.12
Ethyl propionate	298.1	275.1	2.44	1.08

[1] Cp. ninth paper.

[2] Cp. sixth and ninth papers.

values is very good in most cases, and it is a general belief that some of these compounds are indeed unassociated. If we now consider the manifestly associated compounds, the method of comparison outlined above gives us a means of calculating the magnitude of the association. For we have seen that the absolute temperature required to produce the given fluidity is directly proportional to the molecular weight. The assumption that this holds true as molecules unite with each other is rather a deduction than an assumption. Its contradiction would involve

TABLE VIII.

A Comparison of the Values of Association as Determined by Different Investigators.

Substance.	R. & S.[1] 16–46°.	R. & S. Corr. by Traube.	Traube.[2] 15°.	Longinescu.[3]	B.&H.[4], Temp. of ($\phi = 200$).
Water	3.55 1.64	1.79	3.06	4.67	2.31
Ethylene chloride	——	——	1.46	1.00	1.21
Dimethyl ketone	1.26	1.18	1.53	1.60	1.23
Diethyl ketone	——	——	——	1.25	1.16
Methyl propyl ketone	1.11	1.10	1.43	1.25	1.14
Formic acid	3.61	2.41	1.80	1.80	2.05
Acetic acid	3.62 2.13	2.32	1.56	1.75	1.77
Propionic acid	1.77	1.45	1.46	1.55	1.57
Butyric acid	1.58	1.35	1.39	1.36	1.51
Isobutyric acid	1.45	1.28	1.31	——	1.51
Benzene	1.01	1.05	1.18	——	1.17+
Toluene	0.94	1.01	1.08	——	1.08+
Methyl alcohol	3.43 2.32	2.53	1.79	3.17	1.84
Ethyl alcohol	2.74 1.65	1.80	1.67	2.11	1.83
Propyl alcohol	2.25	1.70	1.66	1.67	1.74
Isopropyl alcohol	2.86	2.00	1.53	——	1.75
Butyl alcohol	1.94	——	——	1.47	1.62
Isobutyl alcohol	1.95	1.53	1.54	——	1.66
Active amyl alcohol	1.97	1.54	1.53	——	1.54
Allyl alcohol	1.88	1.50	1.55	1.80	1.69
Methyl formate	1.06	1.07	(1.60)	1.12	1.25
Ethyl formate	1.07	1.08	$1.39_0°$	——	1.19
Methyl acetate	1.00	1.04	$1.48_0°$	1.09	1.17
Ethyl acetate	0.99	1.04	1.25	1.00	1.12
Propyl acetate	0.92	1.00	1.31	1.00	1.11
Ethyl propionate	0.92	1.00	1.27	0.94	1.08
Methyl butyrate	0.92	1.00	$1.30_0°$	1.00	1.10

[1] Ramsay and Shields, Zeitschr. f. physik. Chem., *12*, 464 (1893); Do., *15*, 115 (1894).

[2] Traube, Ber. d. deutsch. chem. Gesell., *30*, 273 (1897).

[3] Journ. Chim. Phys., *1*, 289 (1903).

[4] Bingham and Harrison, *loc. cit.*

an assumption for which we do not at present see any justification. The average molecular weight or association of a liquid is therefore measured by the ratio of the observed absolute temperature to the calculated absolute temperature at the fluidity chosen as the basis of comparison.

The observed and calculated absolute temperatures corresponding to the fluidity of 200 and the calculated association of some supposedly associated compounds are given in Table VII. The slopes of these compounds are also given in the fourth column.

In Table VIII. is given a comparison of the association as calculated by the fluidity method with that obtained by other methods.

So far as one is able to judge, the result seems to be all that could be desired. We believe that the fluidity method is freer from assumptions to which question may be raised, than the other methods, and we hope that it may prove of use in calculating association. However that may be, it seems certain that the above concordance ought to add very greatly to the weight of the reasoning of this paper as a whole; for it is especially to be noted that similar results have not and probably cannot readily be obtained from a comparison of viscosity data as such. Lest this statement appear unsupported, we shall attempt to prove it as follows. Let AB and $A'B'$ in Fig. 19 represent two fluidity curves, parallel to each other and therefore presumably representing members of the same class of substances, and let a third fluidity curve CD be at an angle to the other two to represent a substance in another class. Since we have elected to compare absolute temperatures at a fluidity of 200, this amounts to comparing the intercepts of the curves on the line AD, whose equation is $\varphi = 200$. The corresponding viscosity curves obtained by taking the reciprocal values of the above fluidities and multiplying by 10,000 are represented by ab, $a'b'$, and cd; and ad is of course the reciprocal of the line AD. But the point a and the point where the curve $a'b'$ crosses ad are points of equal slope on the viscosity curves, hence we conclude that within a given class it makes no difference whether we compare temperatures corresponding to a given fluidity or temperatures corresponding to a given slope on the viscosity curves. The latter is exactly the method of comparison which Thorpe and Rodger found very advantageous. But between different classes they found difficulties.

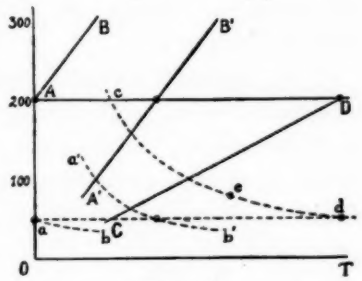


Fig. 19.

Diagram illustrating the relationship between viscosity and fluidity-temperature curves.

This is now easily explained, for d is the reciprocal of the point D which we believe should have been used; but they selected the point e, which has the same slope as the point a, and for this choice we think that there is not adequate reason. However it is advantageous for our point of view that they unwittingly proved that a comparison of temperatures corresponding to a given fluidity gives the best results even if they did not make it perfectly general.

Fluidity and Hydration.[1]—It is but a step from the consideration of the complexes which exist in homogeneous liquids to that of the loose combinations in solution, which are most common in aqueous solutions and are called hydrates. An increase in the average molecular weight usually, but not necessarily invariably, takes place and this increase should under favorable circumstances be capable of detection and measurement by means of the fluidity method.

The queston of hydration was in the minds of the earliest investigators in the field of viscosity, hence it is useless to hope to add anything of moment to their work without an advance in the underlying theory. Our study of the problem has led to the belief that there are three misconceptions prevalent, which have stood in the way of its solution.

1. It has invariably been assumed that viscosities and not fluidities are additive, causing the simplest mixtures to appear abnormal, as already discussed.

2. By common consent the concentrations of solutions have been reckoned on the weight-percentage or molecular percentage basis. But we have already pointed out that concentrations must be reckoned in terms of volume percentage, since it is the total space occupied by a liquid of given fluidity which is of importance, and not its density or molecular volume.

3. It has been assumed that a maximum, or minimum, in a viscosity curve had peculiar significance and that it coincided with the composition of the hydrate formed. Neither part of this assumption appears to be true, as we shall now attempt to prove by the consideration of the following simple cases.

Case I. The fluidity-temperature curves of two similar substances are represented by A and B in Fig. 20*a*. Let it be supposed that a combination takes place between the two substances on mixing, which is a maximum in the 50 per cent. mixture; so that for this mixture the fluidity is lowered from the curve C (dotted), which would be expected were there no combination, to the curve $.5B$. Plotting these points, the fluidity-concentration curves of these same substances for the various

[1] Cp. fourteenth paper.

temperatures t_1, t_2, t_3, etc., may be interpolated as shown in Fig. 20*b*. The curves .25*B* and .75*B* may be added to Fig. 20*a* for the 25 per cent. and 75 per cent. mixtures respectively. In this case there is a well-defined

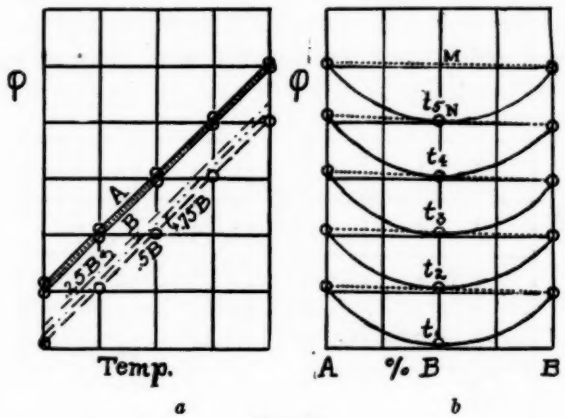


Fig. 20.

minimum in the fluidity-concentration curves in the 50 per cent. mixture corresponding to the composition of the hydrate.

Case II. In Fig. 21*a*, the same conventions are employed, the curves *A* and *B* being still parallel and the maximum lowering of the fluidity

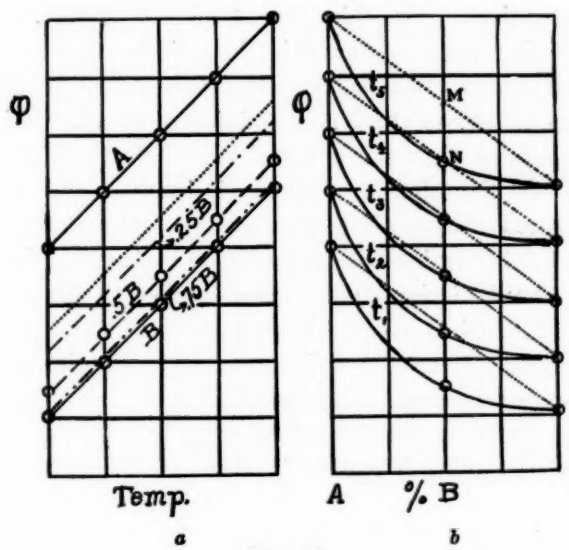


Fig. 21.

being in the 50 per cent. mixture and the same in amount as in Case I. The only difference is that the two curves *A* and *B* are sufficiently

distant from each other so that the curve .5*B* falls above the curve *B*. The result is that the fluidity-concentration curves, shown in Fig. 21*b*, no longer give a minimum, although by assumption the hydration is the same as before both in relative composition and in amount. However it is clear that the deviation of the fluidity-concentration curves from the linear curves, which would be expected were there no combination, and as measured vertically *MN*, is the same as in the preceding case.

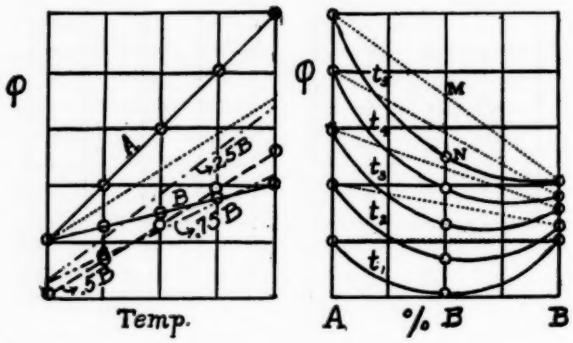


Fig. 22.

Case III. In Fig. 22*a* and *b* is depicted the case where the fluidity-temperature curves of the components are no longer parallel so that the result is practically a combination of cases I. and II. At low temperatures there is a good minimum in the fluidity-concentration curves, but it gradually shifts to the right as the temperature is raised, until at the highest temperatures there is no minimum at all. It is manifestly erroneous to assume that the composition of the hydrate changes on this account. On the other hand the deviation from the expected linear curves as measured vertically is everywhere the same as in the simpler cases.

In practice the hydration will generally be less at the higher temperatures so that the deviation should grow smaller as the temperature is raised, but the cases given are perhaps sufficient to show that the *deviation* of the observed fluidity-concentration curve from the linear curve, which would be expected were there no combination between the components of the solution, can alone furnish trustworthy information.

If the above reasoning is correct it seems possible that the way may now be open to use the property of fluidity to throw important light upon the question of hydration and other similar combination in solution. For example, certain puzzling contradictions may be immediately disposed of. Thorpe and Rodger[1] measured the viscosities of mixtures

[1] J. Chem. Soc., 71, 366 (1897).

of methyl iodide and carbon disulphide and of carbon tetrachloride and benzene at several temperatures. In each case they found sagging in the viscosity curves, which they accounted for by assuming that the components of the mixtures united with each other to some extent. But they themselves noted that when methyl iodide and carbon disulphide are mixed, quite a marked expansion takes place, with the absorption of heat. With carbon tetrachloride and benzene there is no expansion but perhaps a very slight contraction. The evidence is therefore puzzling if not absolutely contradictory. When the fluidities of these pairs are plotted against volume concentrations, on the other hand, we find that the curves are slightly bent upward in the case of methyl iodide and carbon disulphide, and slightly sagged downward in the case of carbon tetrachloride and benzene. Moreover the sagging in the latter case is greatest at the lower temperatures where the conditions are most favorable to combination. This is shown by the continuous curves in Fig. 23. The curves indicated by dashes represent the result of plotting fluidities against the weight concentrations as given by Thorpe and Rodger. The result is contradictory, because an increase in fluidity would not be expected to accompany even a very slight contraction. Moreover the departure from the linear (dotted) curve, which we should expect if there were no combination, should not increase as the temperature is raised as is apparently the case. For an increase in fluidity in the mixture would seem to be due to one component causing

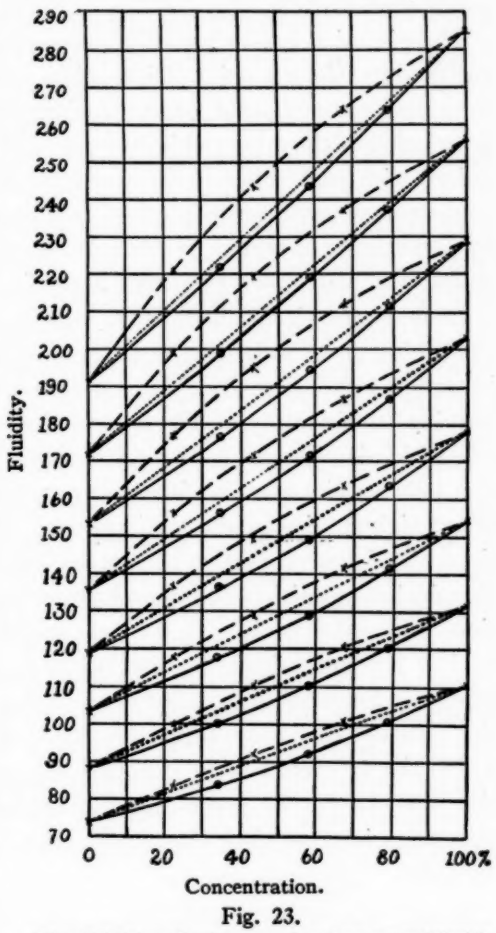


Fig. 23.

The fluidities of mixtures of carbon tetrachloride and benzene plotted against volume concentrations (continuous lines) and weight concentrations(dashes) as compared with the linear curves (dotted).

the destruction of the association of the other, and this effect would naturally be greatest at low temperatures where the association is greatest. Fortunately these contradictions are cleared up as we have seen by plotting fluidities against volume-concentrations, for which there is ample justification.

The viscosity curves for chloroform and ether as measured by Thorpe and Rodger[1] show a point of inflection. To explain this they were forced to assume that at some concentrations one of the liquids destroyed the association of the other, while at other concentrations the two components united with each other to form complexes. On its face this assumption seems somewhat improbable and this improbability is further increased by other facts obtained by the same experimenters. For in the case of chloroform and ether there is "a considerable evolution of heat and a notable contraction," the greatest contraction taking place in the mixture containing 40.14 weight percentage of ether. But the point of inflection in some of the viscosity curves occurs in this mixture, the exact point varying considerably as the temperature is raised. So viscosity tells a tale which is different from that of any of the other properties, and this fact tells heavily against viscosity comparisons as an aid in investigation. When rightly viewed the testimony of all of the properties must agree, since all of the properties of a substance must be the outgrowths of its chemical composition and constitution together with the physical conditions imposed upon it. In the case under discussion, if we plot fluidities against concentrations, we obtain curves for the different temperatures, which no longer show a point of inflection, but are considerably sagged, the greatest deviation from the linear curve occurring in the mixture where the greatest contraction and presumably the greatest heat evolution also occur. Thus the different kinds of evidence agree in indicating that there is some kind of a combination between the components of the mixture.

Were the components of the mixture non-associated, it would not be difficult to calculate the average molecular weight of the mixture by the fluidity method. But substances which form the feeble combinations on mixing which we have under consideration are usually associated and it is quite likely that this association is altered in the mixture, so that the result is considerably complicated thereby. This change in the association of the components may indeed shift the point of greatest deviation from the linear curve, so that this point will not exactly correspond to the composition of the hydrate. The familiar problem of hydrates in aqueous solution is therefore a complicated one, which we

[1] Loc. cit.

are not yet in a position to handle very satisfactorily, although it does seem possible to clear the way for a solution. To fix our attention upon this problem more closely, let us consider the case of ethyl alcohol and water. The former at the fluidity of 200 requires an absolute temperature of 343.6 and has an average molecular weight of 1.83 times the empirical formula. The latter requires an absolute temperature of 328.9 and the association is 2.31. With ethyl alcohol and water there is a definite minimum in the fluidity curves, which at some temperatures occurs in the mixture corresponding to the composition $C_2H_6O.3H_2O$, *i. e.*, about 52 volume per cent., hence earlier workers on the viscosity of these mixtures concluded that this hydrate is actually formed. The greatest deviation from the linear curves, which would be expected were there no combination, occurs in the mixture which corresponds to the hydrate $C_2H_6O.4H_2O$, or in the mixture containing 44.79 volume per cent. of alcohol. It has been objected that the maximum in viscosity (or the minimum in fluidity) migrates as the temperature is changed, but so far as we have been able to observe, this is not true of the maximum deviation from the linear curves.

On mixing, it seems altogether likely that the diminished frequency of collision between molecules of the same kind will lessen the tendency toward association. Whether this action occurs and whether it obeys the law of mass action can probably be determined and will be discussed later. But for the moment let us consider this breaking down of association as negligible.

The temperature corresponding to a fluidity of 200 in the 52.08 volume per cent. mixture which we should expect were there no combination, would be $.4479 \times 343.6 + .5521 \times 328.9 = 335.5$. On the other hand, from the constants already given, the temperature required to give the pure hydrate $C_2H_6O.4H_2O$ a fluidity of 200 would be $14 \times 59.2 + 5 \times 24.2 - 2 \times 95.7 = 758.4$. But the observed absolute temperature at which the 44.79 volume per cent. mixture has a fluidity of 200 is 362.3. Hence if we let x represent the fraction of the volume of the mixture combined as $C_2H_6O.4H_2O$, the rest remaining unchanged, we have $335.5 (1 - x) + 758.4x = 362.3$ or $x = 0.06337$. But this value has no great significance for the following reasons.

1. It has been assumed that the hydrate has the simplest possible formula, but it may be a polymer of the value given. This would make the percentage of hydration lower than that given.

2. The association of the components may be less after mixing. This would raise the percentage.

3. In mixtures other than the one considered, the percentage of hydration would certainly be different, if the law of mass action applies.

It may now be shown that the hydrates in solution are qualitatively at least subject to the law of mass action. The mixture of alcohol and water in the ratio corresponding to $C_2H_6O.3H_2O$ has at 25° C. a fluidity of 42.5 and a mixture of acetic acid and water corresponding to $C_2H_4O_2.H_2O$ has at 25° C. almost exactly the same fluidity; so that were there no chemical change, these two mixtures might be combined with each other in any proportion without altering the fluidity. But we have noticed that when acetic acid and ethyl alcohol are mixed there is a drop in the fluidity and we may remark in passing that this cannot be due to the formation of ethyl acetate, because this substance has a high fluidity—236.3 at 25°. However, the dilution of the mixture of alcohol and water by adding acetic acid will cause a marked decrease in the amount of combination between the alcohol and water, because according to the law of mass action four molecules of water must meet a molecule of alcohol in order to form a hydrated molecule, and the presence of the acetic acid lowers the concentration of the water. As a matter of fact, the fluidity of the mixture is raised by 10 per cent. above the expected 42.5 or less, if this law had been inoperative. This is not the only possible explanation of the increase in fluidity in this case. It may be due to the dissociation of the acetic acid on dilution.

The same point may have light thrown upon it from another source. The values of μ_∞ measure the sums of the velocities of the cations and anions $u + v$ in ionic migration. In mixtures of alcohol and water these values suffer a gradual falling off as the percentage of alcohol is increased, but there is no minimum to correspond with the minimum in the fluidity of the mixtures. The reason seems to be that in the mixture with the smallest fluidity, the components of that mixture are united with each other to their very fullest extent, hence the "atmosphere" around the ion is reduced to the smallest amount and the migration velocity is therefore relatively large. If the atmosphere about the ions were uniform in size, conductivity would be directly proportional to the fluidity of the solution.

Since writing the above, an instance has occurred to us where two apparently slightly associated substances unite with each other with considerable vigor to form complex molecules, which seems to give us the simplest possible case for determining whether the formation of solvates follows the Law of Mass Action. Thorpe and Rodger [1] in studying mixtures of ether and chloroform, noted that there is a considerable heat evolution and contraction on mixing. So far as we can learn from their measurements, the maximum contraction occurs in a mixture con-

[1] *Loc. cit.*

taining less than 40 per cent. of ether by weight and perhaps less than 39 per cent. The maximum deviation of the fluidity-volume-concentration curve from the linear curve occurs in the 58 volume per cent. mixture ± 3 per cent. This corresponds to about 39.8 per cent. by weight. A mixture corresponding to the composition $C_4H_{10}O.CHCl_3$ contains 38.30 per cent. of ether by weight. Guthrie[1] has noted that the greatest heat evolution occurs in the mixture of equimolecular proportions and that the vapor-pressure curve of the mixtures gives confirmatory evidence of the formation of a compound with the formula corresponding to $C_4H_{10}O.CHCl_3$.

Since the evidence afforded by the different properties of mixtures of ether and chloroform was formerly conflicting, it is a source of great satisfaction and confidence that so many lines of evidence are absolutely in agreement in pointing to the formation of a definite compound. The reluctance which chemists have toward recognizing this class of compounds has no doubt been due partly to the fact that the compounds themselves cannot usually be isolated, and furthermore the mixture does not act like a chemical compound in that it maintains the properties of all of the original components. This however is doubtless due to there being a dynamic equilibrium between the compound and the original components. Nevertheless recognition will not be given to this large class of compounds, until their presence and properties can be quantitatively established. Fortunately in the case of ether and chloroform, this information seems available.

In the mixture containing 56.26 per cent. by volume of ether corresponding to one molecule of ether to one molecule of chloroform we may calculate the percentage combined as follows. From the atomic constants we find that the compound $C_4H_{10}O.CHCl_3$ should have a fluidity of 200 at the absolute temperature of 538.6°. But actually we find that a mixture of this composition has a fluidity of 200 at 282.9° absolute. Pure ether and pure chloroform have fluidities of 200 at 216.5° and 305.3° respectively, so that if the mixture were wholly uncombined, the absolute temperature necessary for a fluidity of 200 would be $216.5 \times 0.5626 + 305.6 \times 0.4374 = 255.4$. Letting x represent the fraction of the volume of the mixture which is combined, we obtain the equation

$$538.6x + 255.4(1 - x) = 282.9,$$

$x = 0.0971$. Since less than ten per cent. of the volume of the mixture is actually in combination, it seems reasonable to assume that a dynamic equilibrium exists between the combined and the uncombined portions. If the Mass Law holds, we have

[1] Phil. Mag., *18* (5), 495 (1884).

$$\frac{[C_4H_{10}O]\,[CHCl_3]}{[C_4H_{10}O.CHCl_3]} = K,$$

where the concentrations are no longer volume but molecular concentrations.

In the above equimolecular mixture, if we let y represent the number of cubic centimeters of ether which are combined in every one hundred cubic centimeters of mixture, the volume of the chloroform combined will be $0.7366 \times 193.4y/74.08 \times 1.526$ where the specific gravities of ether and chloroform are taken as 0.7366 and 1.526 respectively and their molecular weights 74.08 and 193.4. Since the sum of the two volumes is 9.71 we find that the volume of the ether combined is 4.30 and of the chloroform 5.41 c.c. Substituting the molecular concentrations in the above formula we obtain for the value of the constant K

$$K = \frac{\left[\frac{(56.26 - 4.30)0.7366}{74.08}\right]\left[\frac{(43.74 - 5.41)1.526}{193.4}\right]}{\left[\frac{9.71 \times 1.1016}{277.52}\right]} = 4.0633.$$

With thsi value of K it becomes possible to calculate the absolute temperature corresponding to a fluidity of 200 for any mixture on the assumption that only one compound is formed and that the Law of Mass Action is obeyed. Thus for a mixture containing 28.21 per cent. by volume of ether, we have, if z is taken to represent the fraction of the volume of the ether which is combined,

$$\frac{\left[\frac{28.21 \times 0.7366}{74.08}(1 - z)\right]\left[\frac{71.79 \times 1.526}{193.4} - \frac{28.21 \times 0.7366}{74.08} \cdot z\right]}{\left[\frac{28.21 \times 0.7366}{74.08} \cdot z\right]} = 4.0633,$$

$z = 0.1162$. The volume of ether combined in 100 c.c. is therefore $28.21 \times 0.1162 = 3.278$ and the volume of the chloroform is $3.27 \times 0.7366 \times 193.4 \div 74.08 \times 1.526 = 4.131$ and the total volume in combination is 7.409 c.c. The volume of the uncombined ether is 24.94 c.c., and of chloroform 68.52 c.c. Hence the calculated absolute temperature corresponding to a fluidity of 200 is $0.2493 \times 216.5 + 0.6766 \times 305.3 + 0.07409 \times 538.6 = 300.4°$. The value read from the curve is 297.4°. Similar remarkable agreement is obtained for other mixtures whose fluidity was measured by Thorpe and Rodger.

We are not quite justified in stating that this proves that the mass law applies to all of those loose combinations which are believed to exist in solution, but it points the way toward a solution of this interesting

question. In the case of highly associated liquids the problem is complicated by the breaking down of this association upon dilution. Other constants are thereby introduced, but it is believed that this difficulty may be overcome. Finally it may be pointed out that this method seems suited for the solution of various problems which have vexed the organic chemists such as the mechanism of esterification. Our experiments seem to indicate that there is a loose combination between the alcohol and acid before the ester is actually formed.

Fluidity Formulas.[1]—Since fluidities are normally additive, the formula expressing the change of fluidity with the temperature in its simplest form should be $\varphi = AT$ or $\varphi = \alpha + \beta T$. This latter form may be deduced from the empirical viscosity formula of Meyer and Rosencranz,[2] $\eta = c/(1 + at)$. But most liquids do not expand equally on heating and it may be that almost all liquids are associated to some extent. However that may be, mercury is the only liquid known which has a linear fluidity curve within the limits of experimental error, over a large range of temperature. The curves of other substances must not cut the temperature axis since we cannot conceive of negative fluidities, yet they must all approach the temperature axis at absolute zero. Therefore we conclude that the fluidity curves must be asymptotic to that axis. At high temperatures the association is broken down and the fluidity curves become more and more nearly linear as we observe to be the case in Fig. 17. A general fluidity equation must therefore incorporate the following properties.

1. It must reduce to a linear equation for the ideal substance.

2. One branch of the curve in its general form must be asymptotic to the temperature axis.

3. At high temperatures the curve must be linear, so that the other branch of the curve must be asymptotic to a line which forms an acute angle with the temperature axis. This will not be true to the critical temperature as indicated later.

These conditions are fulfilled by the equation.

$$t = A\varphi - \frac{B}{\varphi} + C, \tag{9}$$

where A, B, and C are constants. This is the equation of a hyperbola, $t_1 = A\varphi$ representing the equation of the ideal substance and $t_2 = C - B/\varphi$ representing the breaking down of association which is complete at the temperature C. An extended study has shown that the average

[1] Cp. seventh paper.

[2] Wied. Ann., 2, 387 (1877).

percentage difference between the observed and calculated values for 85 substances with some 1,000 duplicate observations is 0.17. If the alcohols are omitted from the calculation, the percentage difference falls to 0.09 for 70 substances.

The best formula heretofore proposed is perhaps that of Slotte,[1]

$$\eta = \frac{c}{(a + t)^n},$$

or in the slightly simplified form of Poiseuille,[2]

$$\eta = \frac{c}{1 + \alpha t + \beta t^2}.$$

From this latter is derived the formula

$$\varphi = A + Bt + Ct^2, \qquad (10)$$

which is the equation of a parabola, and hence may be debarred at once since it does not meet the conditions of a general equation that it must be asymptotic to the temperature axis and to a line at an acute angle to this axis As a matter of fact, it has been found that this equation does not apply at all to the alcohols where the fluidity curves depart most widely from linearity. The average percentage deviation between the observed and calculated values with Slotte's equation applied to 64 substances is 0.15. The alcohols were excluded because Slotte's formula breaks down entirely when applied to them.

By introducing a fourth constant into our equation a much better agreement may be obtained, while keeping the general properties of the equation the same. Thus with the equation

$$t = A\varphi - \frac{B}{\varphi + D} + C \qquad (11)^3$$

eight substances which gave an average percentage difference between the observed and calculated values of 0.77 with equation (9), with equation (11) give a percentage difference of only 0.07.

Fluidity and Volume.[4]—Evidence from several different quarters points to a relation between fluidity and volume in liquids.

1. We have seen that the association of liquids may be calculated from the fluidity, and Traube[5] has calculated the association from the volume. There is therefore a connection between the two and it is

[1] Wied. Ann., *14*, 13 (1881).
[2] Pogg. Ann., *58*, 424 (1843).
[3] Cp. seventh and ninth papers.
[4] Cp. third, sixth, and ninth papers.
[5] *Loc. cit.*

evidently possible to calculate the volume of a compound from its fluidity and *vice versa*.

2. Again we have seen that in mixtures a contraction in volume is usually accompanied by a decrease in fluidity.

3. In pure liquids an increase in the temperature is usually accompanied by an increase in both the volume and the fluidity. Water and sulphur are exceptional.

4. Pressure usually decreases both volume and fluidity. Water is again exceptional at certain temperatures.

5. If we regard the pressure as constant as is the case in ordinary viscosity measurements, then van der Waals' equation

$$\left(p - \frac{a}{v^2}\right)(v - b) = RT$$

may be written

$$T = \alpha v - \beta - \frac{\gamma}{v} + \frac{\delta}{v^2} \qquad (12)$$

where α, β, γ, and δ are constants. This equation expressing the relation between the volume and temperature is the same in form as our equation (9) for expressing the relation between the fluidity and the temperature, except for the term δ/v^2, which is of minor importance. It follows therefore that fluidity and volume are either dependent upon some more fundamental property or upon each other, and that quite similar formulas may be used to represent the effects of the temperature upon both. Further work needs to be devoted to such relationships.

Nature of Viscous Resistance.[1]—As regards fluidity, gases and liquids afford a sharp contrast. In liquids the fluidity generally increases with the temperature, while in gases the fluidity decreases with the temperature, so that at the critical temperature the fluidity apparently passes through a maximum. In gases the fluidity is independent of the density, while in liquids the density, as we have already seen, is of prime consideration. This contrast suggests that the origin of these losses of energy must be different in the two cases.

In gases, the particles of one layer penetrate another layer with lower translational velocity and thus the uni-directional motion becomes changed into irregular molecular motion or heat. This loss increases with the temperature because the motion of the molecules is thereby increased. So long as the volume of the molecules themselves is negligible and the molecular free path is small in comparison with the dimensions of the containing vessel, it appears that as the density of the gas

[1] Cp. tenth paper.

is increased, the increase in the loss of energy due to the greater number of molecules crossing a given plane surface in a unit of time, is exactly compensated by the decrease in the loss of energy due to the smaller depths from which the molecules have come, so that the viscosity is independent of the density.

In liquids the molecules themselves have such large volume in comparison with the spaces between them, that the excursions of the molecules are short and the cause of the loss of energy which is powerful in gases is of relatively small significance. On the other hand, as one layer of liquid moves over another, collisions will frequently be caused by the molecules of one layer overtaking and colliding with the molecules of the more slowly moving layer, and these collisions will cause a loss in translatory motion. Increasing the density either by lowering the temperature or increasing the external pressure will increase this effect.

It has been customary to ascribe the viscous resistance of liquids to the attraction between the molecules. In the opinion of the author, cohesion and fluidity are indeed related but not as cause and effect. Since the cohesive forces within the liquid are balanced, it is difficult to see how work can be done against them as one layer of liquid moves over another. Space will not now permit going further into this interesting and important subject.

The Fluidity of Solids.[1]—It has been assumed by some investigators that the damping of the vibrations of a wire, after allowing for the friction of the air and the loss of energy to the support, is a measure of the viscosity of the solid. To the present writer, it seems probable that while this loss of energy is a true viscous effect, the amount of the damping cannot for a moment be considered *directly* proportional to the viscosity of the substance. Such an assumption would lead us to the absurd conclusion that lead is less fluid than steel or quartz, since the damping in lead is very rapid. Moreover, since the rate of damping increases with the temperature, it would force us to conclude that solids are analogous to gases, in that the fluidity decreases as the temperature is raised, even though we recognize that amorphous solids are nothing but undercooled liquids. The truth is probably quite the opposite of this common assumption. Lead is of course more fluid than steel and the fluidity of both increases with the temperature, and the rate of damping is rather a measure of the *fluidity*. In bending a "perfectly elastic substance," the molecules do not move over one another, but merely move about in the spaces between the molecules, causing strains to be set up. Therefore as soon as the stress is removed the strain disappears without

[1] Cp. tenth paper.

loss of energy by means of internal flow. But since these spaces are small, the elastic limit is soon reached, beyond which rupture or viscous flow must take place. In ordinary solids there is some flow of the molecules over each other as stress is applied, so that when the stress is removed the material does not fly back at once to its old position, but appears temporarily to be considerably distorted—the "elastic after-effect"—and *is* permanently distorted to a very much slighter extent. The rate of damping is then a measure of the viscous flow or fluidity. This conception may be used to explain many of the curious facts in connection with elasticity.

The Molecular Weight of Solids.[1]—Amorphous solids are to be regarded as liquids and hence there is no inherent reason why their molecular weights may not be obtained by the fluidity method as soon as sufficient data are accumulated for the purpose. When such undercooled liquids change to crystalline solids, the fluidity usually drops to but a small fraction of its former value. This indicates a great increase in apparent molecular weight which it seems possible to calculate by the method already given, but the viscosity data necessary for such calculation are lacking.

Conclusions.—Upon the relations between fluidity and physical and chemical properties we may add the following to the conclusions already given:

17. The fluidities of unassociated substances of a homologous series at their boiling-points are a linear function of their boiling temperatures.

18 The above relation is true of other vapor-pressures than that of the ordinary boiling temperature, and it may be made evident in various ways. For example, the fluidities of the ethers are nearly identical at their boiling-points, so by plotting fluidities against vapor-pressures corresponding to the same temperatures, a single curve is obtained for the whole class of substances. Or by taking one substance as a standard and multiplying the fluidities of other substances by the ratio of the fluidity of the latter at their boiling-points to the fluidity of the standard at its boiling-point, "reduced fluidities" are obtained. Employing the fluidity-vapor-pressure curve of the standard substance, vapor-pressures may be calculated from the reduced fluidities. It is found that the calculated values of vapor-pressures of over 10 cm. for about 20 substances differ from the observed values by a little over 3 per cent.

19. There is shown to be a relation between fluidity and chemical composition. The fluidity-temperature curves of a given class of compounds consists of a family of nearly straight and nearly parallel lines.

[1] Cp. tenth paper.

Hence the slope of the curves is characteristic of the class and their intercepts are indicative of the molecular weight, and of constitutive influences to a very much lesser degree. Evidence is given to show that absolute temperatures corresponding to a given fluidity form a proper basis of comparison. Constants obtained for a given fluidity enable us to calculate the absolute temperatures of many other substances at that fluidity. For 35 substances, the calculated values differ from the observed by less than 0.8 per cent.

20. Since fluidity gives a means for calculating the molecular weights of liquids it is evidently possible to use the method for calculating association, the association being the ratio between the observed absolute temperature corresponding to the fluidity used as a basis of comparison and the absolute temperature as calculated from the constants. A comparison of values of association by the fluidity method and the methods of Ramsay and Shields, Traube, and Longinescu for 27 substances shows as satisfactory an agreement as can well be expected.

21. Reasons are given why similar relations to those here given between fluidity and vapor-pressure, fluidity and chemical composition, and fluidity and association have not been and cannot readily be worked out by comparing viscosities instead of fluidities.

22. The fluidity method of calculating molecular weights may evidently be extended to the case of mixtures where the components unite in loose combinations as in hydration. The theory demands that the solutions be reckoned in terms of volume percentages and not in weight or molecular percentages, as is often done. It is proved furthermore that the occurrence of a maximum or minimum in a viscosity or fluidity curve does not necessarily indicate the composition of the solvate, and the shifting of a maximum or a minimum does not necessarily indicate a change in the composition of the solvate. Theory indicates that the point in the fluidity-concentration curve where the deviation of the fluidity curve from the linear curve, which would be expected were there no solution, is a maximum, may give us knowledge of the composition of the solvate. Evidence is given to show that solvation follows the law of mass-action, and the method is given of calculating the percentage of the mixture which is combined.

23. The properties of a general formula to represent the changes in the fluidity of a substance with the temperature are given, and the formula

$$t = A\varphi - \frac{B}{\varphi} + C$$

where t = temperature absolute, φ = fluidity, and A, B, and C are

constants, is proposed, which has these general properties. This formula may be used to reproduce the observed values of 85 substances tested with an average percentage difference of 0.17. Another constant added to this equation reduces this already small percentage difference very much further.

24. Reasons are given for the belief that there is a close relation between the fluidity of a liquid and its volume:

(*a*) When liquids are mixed, a decrease in volume is generally accompanied by a decrease in fluidity, and the greatest decrease in both appears to coincide in the same mixture. The opposite seems to be true when liquids expand on mixing.

(*b*) Pressure generally decreases both volume and fluidity, and increase in temperature generally increases both.

(*c*) Association may be calculated from fluidity data, and Traube has also calculated association from volume.

(*d*) The above equation is almost exactly the relation between temperature and volume implied in van der Waals' well-known equation.

25. The nature of viscous resistance is discussed, and it is pointed out that while the kinetic theory explains the cause of viscosity in gases, it does not explain it in liquids. The usual assumption, that the viscosity of liquids is due to the attractions between the molecules, is insufficient. A theory is outlined which makes the volume of the molecules themselves the most important factor, the loss of energy arising from the collisions, due to their translatory motion, of the molecules of one layer with the molecules of adjacent but more slowly moving layers.

26. It is indicated that many of the phenomena of elasticity in solids may be explained on the basis of their fluidity. The rate of damping of a wire is probably directly proportional to the *fluidity* of the solid, and *not* to the viscosity, as has often been assumed. The "elastic after-effect" is, according to this view, caused by partial flows in the solid which cause a state of strain to remain after the deforming stress has been removed. This state of strain has been observed in the viscous flow of very viscous liquids like pitch.

27. A possible method for calculating the molecular weights of solids is suggested.

RICHMOND COLLEGE,
RICHMOND, VA.,
June 27, 1912.

AN ABSOLUTE DETERMINATION OF THE VISCOSITY OF AIR.

BY LACHLAN GILCHRIST.

IN view of the recent work of Professor R. A. Millikan, of the University of Chicago,[1] the accuracy with which the elementary charge can be determined is limited only by the accuracy obtainable in the measurement of the absolute value of the coefficient of the viscosity of air. It is of the utmost importance therefore for this reason, and also in view of the recent work that has been carried out on the relation between temperature, pressure and viscosity, that the absolute value of this constant be determined with all possible precision. Professor Millikan had already been led by a careful study of existing data to the conclusion that the present uncertainty in η for air at 25° C. could be still further reduced by new work with a constant deflection method since this method is exceedingly direct and simple and seems more suitable for the absolute determination of η than are either the capillary tube or oscillating body methods. At his suggestion therefore and with his assistance the following apparatus was designed. The results show that the method is capable of measuring η with an uncertainty which does not exceed .2 per cent.

The constant deflection method does not appear to have been used carefully in a direct determination of η for air except by Zemplen.[2] He used concentric spheres separated by a small distance and his results are much higher than those which have been obtained in any trustworthy experiments in this field.

In the present work it was decided to use concentric cylinders for two reasons.

1. It appeared to be the simplest method and the one in which the sources of experimental error could be most readily reached and their effect minimized.

2. The theory associated with the method is simple and the formula which is derived is exact.

[1] PHYS. REV., Vol. XXIII., No. 4, April, 1911.

[2] Annalen d. Phys., 29, 5, pp. 869–908, Aug. 10, 1909; 38, 1, pp. 71–125, May, 1912.

A. Theory.

The theory shows that

$$\eta = \frac{\pi\varphi I(b^2 - a^2)}{a^2b^2T^2\omega l},$$

where η = the coefficient of viscosity.

I = the moment of inertia of the suspended body about the line of suspension.

T = the period of oscillation of the suspended cylinder.

φ = the angular displacement of the suspended cylinder.

a = the radius of the inner cylinder.

l = the length of the inner cylinder.

b = the radius of the outer cylinder.

ω = the constant angular velocity of the rotating cylinder.

The inner cylinder itself was used to determine I and T, and φ was determined by a mirror and scale and a telescope for observation.

Then

$$\eta = \frac{stK}{dT^2},$$

where d = the distance of the scale from the mirror.

$s = 2\varphi d$, that is, the observed deflection of the scale image.

$t = 2\pi/\omega$, that is, the time of one rotation of the outer cylinder.

Now it was hoped from the use of a bifilar suspension to diminish such errors as are due to fatigue or stretching of the suspension.

With such form of suspension the expression for the period is

$$T = \frac{2\pi k}{\alpha}\sqrt{\frac{l}{g}},$$

for small oscillations, where k is the radius of gyration of the cylinder.

α = one half the distance between the strands of the suspension.

l = the length of the suspension.

g = the gravity constant.

A consideration of these formulæ suggested the form of construction and the dimensions used in the following apparatus:

B. Experimental Arrangements.

Figure 1. Main Apparatus.

F, the inner cylinder with suspension and mirror M attached.

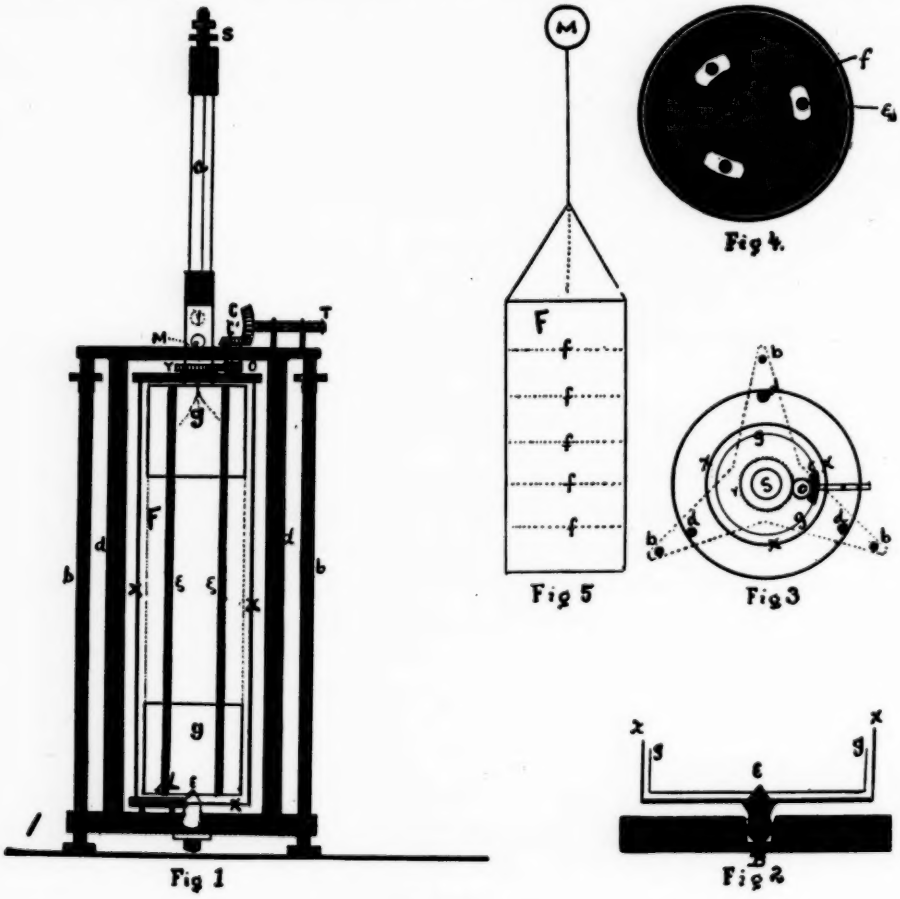
The length of the inner cylinder = 24.88 cm.

The outside radius of the inner cylinder = 5.342 cm.

The length of the suspension = about 25 cm.

This cylinder was made of brass, the wall being made as thin as possible to diminish the mass. The wall was supported by sheets of aluminium as shown in Figs. 5 and 4, *ff*.

The wall of the cylinder was made parallel to the line of suspension in the following manner: The center of the upper aluminium sheet was



Figs. 1–5.

carefully determined to within .1 mm. A fine steel wire suspension was temporarily attached at the center of the upper sheet and the cylinder weighted until the wall at all points was parallel. This was tested with a plumb square to which a very sensitive level was attached. Then three aluminium supports for the permanent suspension were fastened to the upper aluminium sheet and just above their junction the point of attachment of the suspension was placed. This point could be readily adjusted to make the line of suspension parallel to the wall of the cylinder.

The mass of the inner cylinder was 320 grams.

S = the screw head to which the suspension was attached.

gg were guard cylinders about 10 cm. long and rigidly attached by three brass rods. These were also rigidly attached to the tube supporting the screw head S. The distance between the guard cylinders was 24.92 cm., leaving .4 mm. between the suspended cylinder and the guard cylinder. The lower guard cylinder engaged the outer cylinder at ϵ as is shown.

a is a glass portion of the tube so that the suspension thread was always in view.

XX = the outer cylinder, *i. e.*, the rotating cylinder. The inner radius = 6.06357 cm.

This cylinder engaged the frame at Y and ϵ as is shown.

The lower bearing is shown in fuller detail in Fig. 2.

$CC'OY$ represent the transmission gear connecting the driving shaft T with the outer cylinder.

L = a level. There were two at right angles to each other.

d = the supports of the frame

b = the levelling rods on which the instrument was supported.

Fig. 2 shows the lower bearing of inner guard cylinder g, the outer cylinder X and the frame B.

Fig. 3. A plan of the top of instrument.

S = the opening through which the tube which contained the suspension passed.

$CC'Oy$ the transmission gear.

g = the inner guard cylinder, as given in Fig. 1.

x = the outer cylinder as given in Fig. 1.

b, d = etc., as given in Fig. 1.

The dotted lines indicate the supporting frame at the top of the instrument.

Method of Measuring Dimensions.

1. *Inner Cylinder.*—The length and diameter were obtained by means of calipers reading to .001 cm. and the average of a large number of readings was taken.

The mass was obtained by means of a balance reading, .1 mg.

2. *Outer Cylinder.*—The diameter was obtained by filling the cylinder with water, weighing the water, noting the temperature and using density tables to get volume, and then calculating the diameter.

3. The time of rotation of the outer cylinder and the period of oscillation of the inner cylinder were obtained by means of a stop watch. This watch was compared with a chronometer which had been regulated to

accord very closely to the clock in the Canadian Government's Observatory at Toronto.

4. The thermometer which was graduated to .1 dg. was compared with the standard thermometer in use at the observatory. A Beckmann thermometer was also immersed in the bath to indicate changes of temperature.

Fig. 2. Other Apparatus.

1. A clock-driving apparatus was used to drive the rotating cylinder. This instrument was of superior type and simple construction. It was driven by weights and could be directly connected by a shaft to the cylinder. It was made by Wm. Gaertner & Co., of Chicago, and was kindly loaned for the experiment. The average error over one hour in the clock did not exceed 1 part in 3,600. When it was loaded and set running the tests for speed agreed to this degree of accuracy.

The period of vibration of the inner cylinder was such that an average error in the rotation of the outer cylinder much larger than this would not seriously affect the steadiness of deflection.

2. A constant temperature bath. This was a water-bath of the kind described in several text-books in physics.

It was heated by incandescent electric lamps and was regulated by a mercury thermostat, a telegraph relay being used to control the make and break of the heating circuit. For temperatures within 10° C. of the temperature of the room when making a determination of η, the bath did not vary .01° C. and not more than .1° C. at 20° C. above the temperature of the room.

3. *The Telescope and Scale.*—The scale was ruled carefully for the experiment by Wm. Gaertner and Co. and the telescope was such that readings to .1 mm. could be made fairly readily.

The complete apparatus was set up in the first place on a stone pier in Ryerson Physical Laboratory, University of Chicago, during the summer of 1910 and subsequently on a stone pier in the basement of the Physics Building, University of Toronto. In this way rigidity and constant temperature were obtained and drafts and other disturbances were eliminated.

C. The Method of Measurement and Observation.

1. The following was the general plan of work including the difficulties which were encountered, and the methods of dealing with them.

The inner suspended cylinder was made plumb with the line of suspension by use of a plumb square. A shift of approximately five divisions in the level corresponded to .05 mm. out of plumb between top and bottom. One tenth of one division on the levels could be observed.

The levelling rods on the instrument were adjusted so that the outside surface of the guard cylinders, *g*, Fig. 1, was aligned with the surface of the inner cylinder. Two short focal length telescopes which were adjustable on the same base were used to observe this condition. The levels on the instrument were then adjusted. There were scales as well as cross hairs in the telescopes. One half of one division on the scale was easily recognized and the distance between the divisions represented .05 mm. motion of the telescope. The cylinder was found to be from .05 to .15 mm., less in diameter than the guard rings, being smaller at lower end than at upper.

The suspended cylinder was set very accurately symmetrical to the guard cylinders in this way. The upper end of the suspended cylinder was made symmetrical with the upper guard cylinder by adjusting the horizontal screws at the upper end of the suspension. Then the lower end was made symmetrical with the lower guard cylinder by the use of the levelling screws. This threw the upper end out a little. It was readjusted, and again the lower end, and so on. It will be observed that this plan really adjusted the instrument to the suspended cylinder which had previously been made plumb. The levels were then made to read properly. Then the suspended cylinder was lowered to rest on the lower guard cylinder one quarter to one half turn of the screwhead being sufficient for this purpose. The mounted telescopes were also used to test the symmetry of the guard cylinder about the axis of rotation. The average variation was about .05 mm.

2. The accuracy of centering of the outer cylinder was tested thus. The surfaces of the guard cylinders and the inner cylinder were put in alignment as in (3) above and the levels *L* adjusted. The suspension tube *a* and the inner cylinder *F* were then removed. An upright rod with arms at each end which were attached perpendicularly to it was inserted through the opening that was left by the removal of the suspension tube. This rod was arranged so that it could be raised or lowered or rotated in a horizontal plane, and by means of a swivel any motion of the lower arm was communicated to the upper arm. The extent of the motion was indicated by a sensitive level attached to the upper arm. The end of the lower arm was held lightly in contact with the inside wall of the outer cylinder by a small weight attached to the upper arm and the cylinder was rotated by the clock driving apparatus. The test for different places in the cylinder showed an average variation of less than .05 mm., the range of variation being very small. The instrument was adjusted and fixed solidly in the bath and the following observations were made, viz., the zero position on the scale, the period of oscillation of the

inner cylinder, its deflected position, the time of rotation of the outer cylinder, and the distance from the scale.

Some difficulty was found with the suspension owing to its elastic properties and the effect of temperature and moisture—silk, rolled and unrolled phosphor bronze wire, and rolled and unrolled steel wire of different sizes were tried. The use of silk was not successful. The others were used both as single strand and as bifilar suspensions and fair results were obtainable with several of the suspensions used, but the phosphor bronze ribbon rolled from wire, .0762 mm. in diameter and used as a bifilar suspension, gave the best results. It was necessary to obtain a suitable deflection for accurate measurement and still maintain constant zero and deflected positions of the cylinder. With several of the suspensions there was a slow drifting of the zero position or a slight unsteadiness of the deflected position. It was found that upon making the suspension bifilar and such that the period of oscillation of the cylinder was long, a very steady deflected position was obtainable. By leaving the instrument in the constant temperature bath for several hours with the inner cylinder suspended the zero position became more steady. It was also arranged that the driving apparatus could be damped so that it commenced slowly and gradually reached the condition of uniform speed. In this way the deflected position was quickly reached and oscillations that otherwise would exist, were eliminated. The measurement of the deflection was then made and the cylinder was gradually let back to the zero position. With this proceedure deflections of more than 600 mm. could be repeatedly duplicated with an error of no more than .3 mm.

In each determination all the observations and measurements were checked by repetition.

II. *The Measurement of the Moment of Inertia of the Inner Cylinder about the Line of Suspension.*

(*a*) The cylinder was suspended by a strand of steel piano wire .36 mm. in diameter from a firmly built support resting on a stone pier. It was set up in a room which was free from drafts and whose temperature was maintained constant to within 5° C. The cylinder was set oscillating for some time. The period was then obtained by counting a large number of oscillations of small amplitudes, noting the full time, and then calculating the time of a complete oscillation.

(*b*) An annular ring with a cross bar of aluminium was made in the workshop of Ryerson Physical Laboratory with dimensions uniform to a high degree of precision. This was placed symmetrically on the cylinder

and the period of oscillation was again obtained, the amplitude of the oscillations being almost the same as those considered in (*a*).

The expression for the period in (*a*) is

$$T_1 = 2\pi\sqrt{\frac{I_1}{G}}, \tag{1}$$

and in (*b*)

$$T_2 = 2\pi\sqrt{\frac{I_1 + I_2}{G}}, \tag{2}$$

where T_1 = period of oscillation of the cylinder alone.
T_2 = period of oscillation of the cylinder and the aluminium ring and bar.
I_1 = moment of inertia of the cylinder.
I_2 = moment of inertia of the ring and bar. This was calculated from the dimensions.
G = the couple constant of the suspension.

From (1) and (2) I_1 was obtained.

(*c*) *Calculation of* I_2.—For the aluminium bar

$$I_2' = M\frac{c^2 + d^2}{3},$$

where M = the mass of the bar = 22.157 grams.
c = the half width of bar = 6705 cm.
d = the half length of bar = 9.2265 cm.

For the aluminium ring

$$I_2'' = M'\frac{e^2 + f^2}{2},$$

where M' = the mass of the ring = 97.3771 grams.
e = the radius of outside edge = 9.2075 cm.
f = the radius of inside edge = 8.1608 cm.

$$I_2 = I_2' + I_2'' = 8002.409.$$

The periods of free oscillation of the cylinder without and with the ring and bar were 19.7183 secs. and 28.239 secs. respectively.

$$\therefore I_1 = 7615.8.$$

Then

$$K = \frac{I(a^2 - b^2)}{4a^2b^2}$$

$$= 7615{\cdot}8\,\frac{[(5.342)^2 - (6.06357)^2]}{4 \times (5.342)^2 \times (6.16357)^2 \times 24.88} = .60027.$$

D. RESULTS.

I. *Measurements of* η.

The coefficient of viscosity was then calculated from the formula

$$\eta = \frac{stK}{dT^2}.$$

In Table I. are given the values obtained with different speeds of rotation. It shows that the experimental method that has been used gives results which are very concordant. Save for the last two observations which deserve less weight than the others owing to the smallness of the deflection, the maximum divergence of any observation from the mean is but .22 per cent. and the average divergence but .1 per cent.

TABLE I.

	t	s	d	T	$st/dT^2 \times 10^7$	$\eta \times 10^7$	Temp.	$\eta \times 10^7$ at 20.2° C. (Calc.).
1	30.89	70	316	150.33	3,027	1,817	20.2	1,817
2	30.88	69.86	316	150.32	3,021	1,813	20.205	1,813
3	30.79	59.92	302.55	142.06	3,021	1,813	20.2	1,813
4	61.74	34.87	316	150.32	3,015	1,810	20.2	1,810
5	61.66	31.74	315.35	147.46	3,015	1,810	20	1,811
6	61.60	30.01	302.55	142.11	3,025	1,815	20.2	1,815
7	61.58	30.04	302.55	142.11	3,027	1,817	20.2	1,817
8	123.44	16.72	315.35	147.26	3,018	1,812	20.1	1,812.5
9	123.22	16.75	315.35	147.32	3,015	1,810	20.1	1,810.5
10	184.96	11.09	315.35	147.31	2,997	1,800	20.1	1,800.5
11	184.88	13.86	301	188.25	3,007	1,805	20.1	1,805.5

These results for η have been reduced (see Table IV., last column) to the value for the common temperature 20.2° C. by the use of the formula used by Professor Millikan[1] for small differences in temperature.

$$\eta_t = .00017856\,[1 + .00276(t - 15)].$$

The most probable value of η at 20.2° C. is obtained as follows: Since the deflections for the higher speeds of rotation are proportionally greater than for the lower speeds the values should be weighted accordingly. Considering also the steadiness of the deflected and undeflected positions in each case it was decided to give the readings the following weights: 1, 2, 3, 4 each 2; 5, 6, 7 each 1.5; 8, 9, 10, 11 each 1.

This gives as a mean value $\eta = 1{,}812\ (2) \times 10^{-7}$, with a probable error less than 1.3×10^{-7}. The total probable percentage error may also be fairly closely estimated. The probable error of observation as here

[1] Reference already given.

calculated is about .14 per cent. Since however for the different measurements which are given the apparatus was in most cases replaced and readjusted this would include the errors of observation in the measurement of s, t, d, T, and the effect on these of the error of adjustment. The errors in the measurement of a, b and l are exceedingly small and together with that in the measurement of the moment of inertia, do not, I believe, exceed .06 per cent. Then the total probable error is not greater than .2 per cent.

II. In order to determine whether this method would give the same temperature coefficient of viscosity as that which has been obtained by the capillary tube method the following observations were made (see Table II.). For the purpose of comparison the values which are obtained by calculation from the formula of S. W. Holman[1] $\eta \times 10^7 = 1715.50 (1 + .00275t - .00000034t^2)$ are also given. This formula has been shown by several experimenters to be very satisfactory and was found by Tomlinson[1] to accord with his results perfectly.

TABLE II.

Temp.	t	s	d	T	$st/dT \times 10^7$	$N \times 10^7$	$N \times 10^7$, Using Holman's Formula (Calc.).
20.2						1,812.2	1,810
24.58	30.86	66.58	316.5	146.28	3,034.5	1,821.5	1,831
31.9	30.86	67.8	316.5	146.25	3,090.7	1,855.2	1,865.4
37.9	30.88	68.15	316.5	145.84	3,126.2	1,876.5	1,892
43.5	30.88	69.49	316.5	145.84	3,126.2	1,913.4	1,919.6

The greatest variation of the observed from the calculated values is .82 per cent. and the curve showing the relationship between η and temperature is not quite so steep as that given by Holman's formula, or by the formula obtained by most of the experimenters with capillary tubes. The range of temperature for my observations is not great enough, however, to give the relationship as closely as is desirable nor are the determinations at the higher temperatures as accurate as that at 20.2° C.

III. *The Effect of Moisture on the Viscosity of Air.*

The following observations were made in order to determine whether the formula for mixtures of gases which is based on the kinetic theory holds for a mxture of water vapor and air.

[1] Reference given in Table IV.

Air which was dried by being passed slowly through phosphorous pentoxide and sulphuric acid was passed for some time into the instrument through a tube reaching to the bottom. Then a determination of the viscosity was made. Some of the air from the instrument was then drawn slowly into a Crova[1] dew point apparatus and the dew point observed.

The results obtained are shown in Table III. For the last three determinations water was passed into the outer cylinder for the purpose of saturating the air. In number 5 only 2 to 3 c.c. were put in and in numbers 6 and 7 water was put in to a depth of about 2 cm.

The Crova dew point apparatus could not be used to show that the air in the instrument was saturated since the temperature of the room was about 18.3° C. and that of the air in the instrument about 20° C.

TABLE III.

	t	s	d	T	Temp.	Dew Pt. Point.	$st_2/dT\times10^7$.	$\eta\times10^7$.
1	3,086	6,557	316.5	145.66	20.02°C.	6.6	3,015	1,810
2	3,088	6,552	316.5	145.34	20.05	11.6	3,026	1,816
3	3,088	6,557	316.5	145.57	20.05	14.1	3,017	1,811
4	3,087	6,546	316.5	145.62	20.02	17	3,010	1,807
5	3,081	6,432	316.5	143.84	20.02		3,026	1,816
6	3,083	6,432	316.5	144	20		3,021	1,813
7	3,086	6,438	316.5	143.82	20		3,034	1,821

Temperature of room = 18.2° C.

From the results in Table III. it does not appear that the presence of unsaturated water vapor in the air has any measurable effect on the coefficient of viscosity at normal pressure. It is noteworthy, however, that the average of the first four results gives $\eta = 1{,}811 \times 10^{-7}$ and the average of the last three, for which the maximum quantity of water was present, and saturation apparently existed, gives $\eta = 1{,}816.5 \times 10^{-7}$. This seems to show an increase of about .3 per cent. This result is smaller than that obtained by Zemplen[2] (viz., .8 per cent.) but agrees more closely with that obtained by Tomlinson. From the Puluj[2a]

[1] See Preston, Theory of Heat.

[2] Reference already given in paper. (See 2 above.)

$$^{2a}\eta = \eta_1 \frac{\sqrt{p_1 + \frac{m_2}{m_1} p_2}}{\left[p_1 + \left(\frac{\eta_1}{\eta_2}\sqrt{\frac{m_2}{m_1}}\right)^{\frac{2}{3}} p_2\right]^{\frac{2}{3}}},$$

where η = coefficient of viscosity of the mixture, $\eta_1\eta_2$ = coefficient of viscosity of the components, p_1p_2 = partial pressures of the components, $p_1 + p_2 = 1$, m_1m_2 = molecular weights of the components.

formula for mixtures of gases there should be a decrease of about 2 per cent. A modification of this formula by Thiesen[1] has recently been shown by Tanzler[2] and Thomsen[3] to hold fairly well for certain gaseous mixtures. For saturated water vapor the formula is not sustained by the results of my experiments. These accord much better, however, with the calculations of Tomlinson by the method of Stokes[4] based on the experiments of Crookes according to which there should be an increase in the coefficient of viscosity of about .2 per cent. Crookes[5] found that the presence of water vapor did not affect the coefficient of viscosity of air until the total pressure was less than half of the normal pressure and for pressures lower than this it was diminished but not as much as is required by the kinetic theory on which the Puluj formula for gases is based. The results of recent experiments on mixtures of gases by Tanzler and by Kleint[6] are as much as 1.3 per cent. higher than the values calculated from the Puluj formula, that is, the variation is in the same direction as that which appears to exist for mixtures of water vapor and air. It is very desirable then to have the work on mixtures of gases carried out with the same proportional partial pressures as have been investigated, but through a range of lower total pressures until at least the critical pressure is reached. Thomsen shows that in the case of the mixtures of gases investigated by Tanzler and by Kleint, the results which were obtained were approximately such as were to be expected from the formula of Puluj, and Schmitt[7] succeeds in making the approximation much closer by means of a correction factor made necessary by the method of experiment which was used, the formula for which had been developed by Knudsen[8] from kinetic theory considerations. This however makes more imperative the necessity for the investigation which has been suggested above.

E. The Work of Other Experimenters.

The results of recent work by the oscillating body and capillary tube methods are given in Table IV. Those of Tomlinson by the former method and of Holman by the latter method, though of more remote date, are also given, as their work shows every evidence of great care and a high degree of precision. The values at 20.2° C. are calculated from the

[1] M. Thiesen, Ver. der Deut. Phys. Ges., 8, 12, 1906, p. 237.
[2] P. Tanzler, Ver. der Deut. Phys. Ges., 8, 12, 1906, pp. 222–235.
[3] E. Thomsen, Ann. d. Physik, 36, 1911, p. 815.
[4] G. F. Stokes, Phil. Trans., Part II., 1889, p. 440.
[5] Crookes, Phil. Trans., Part II., 1889, p. 427.
[6] F. Kleint, Ver. der Deut. Phys. Ges., 7, 1905, pp. 145–157.
[7] K. Schmitt, Ann. d. Physik, 4, 30, 1909, pp. 393–410.
[8] M. Knudsen, Ann. d. Physik, 4, 28, 1909, pp. 75–130.

TABLE IV.

Experimenter.	Method.	Temp.	Result $\times 10^7$.	Value at 20.2° C. $\times 10^7$.	References.
1. S. W. Holman	Capillary tube			1,810	Phil. Mag. (5), 1886, p. 199. $\eta = .00017155. (1 + .002751t - .00000034t^2)$
2. W. J. Fischer	Capillary tube			1,807	PHYS. REV., 28, p. 104.
3. J. H. Grindlay and A. H. Gibson	Capillary tube	18.94	1,802.7	1,809	Proc. Roy. Soc., A, 80, 1908.
4. A. O. Rankine	Capillary tube	10.6	1,767	1,814	Proc. Roy. Soc., A, Vol. 83, 1910, p. 522.
5. Rapp	Capillary tube	26.	1,838	1,810	Not yet published.
6. Breitenbach	Capillary tube	15.	1,817	1,833	Wied. Ann., LXVII., 1899, p. 803.
7. Schultze	Capillary tube	15.	1,811	1,837	Ann. d. Phys., Vol. 5, 1801, pp. 166–169.
8. Markowski	Capillary tube	15.9	1,814	1,835	Ann. d. Phys., Vol. 14, 1904, p. 742.
9. Tanzler	Capillary tube	15.	1,812	1,838	Ver. der Deut. Physik. Gesell., 8, 12, 1906, pp. 222–235.
10. H. Tomlinson	(*a*) Oscillating pair of cylinders.	12.65	1,774	1,811	Phil. Frans., Vol. 177, Part II., 1886, pp. 767–789.
	(*b*) Oscillating pair of spheres.	9.97	1,762	1,812	
	(*c*) A single oscillating cylinder.	11.78	17,711	1,812	
11. J. L. Hogg		17.33	1,794	1,808	Am. Acad. Proc., 40, 18, 1905, pp. 611–626.

values actually obtained. For all except that of Holman and Fisher the mean values for temperatures near 20.2° C. were taken and the transformation was made by means of the formula used by Millikan.

The Holman and Fisher values are calculated from their final formulæ.

The results are grouped as follows:

(*a*) Those which are obtained by the capillary tube method in which the tubes that were used were fairly large and the results obtained were concordant and agree well with the result obtained by me. (See nos. 1–5.)

(*b*) Those which were obtained by the capillary tube method in which the results, though fairly concordant differ considerably from those of the others. (See nos. 6–9.)

(*c*) Those which were obtained by the damping of a simple pendulum in which all or nearly all of the loss of energy is due to the pushing of the air. (See nos. 10, *a* and *b*.)

(*d*) The damping of torsional vibrations where the complete loss of energy is due to *dragging*. (See nos. 10, *c*, and 11.)

It will be seen from the table that in the work with capillary tubes the results obtained by Breitenbach, Schultze, Markowski, Tanzler and Schmitt are somewhat higher than those of Holman, Fisher, Grindley and Gibson, Rankine, and Rapp, through the determinations by both groups seems to have been made with equal care. With the oscillating body method exceedingly careful work has been done by Tomlinson and recently by Hogg. Their results are concordant but differ considerably from that of Reynolds[1] who used a similar method. In view of the care with which the work has been done it would appear that the discrepancies can only be accounted for by the fact that there are factors in these methods, the effects of which are somewhat indefinitely determinable and therefore have not been uniformly estimated.

It may be well to point out some of the difficulties and sources of error associated with each method and which may to some extent account for the difference in results.

1. *Variations in the Form of the Bore.*—The following will illustrate. The equation giving the coefficient of viscosity for a tube of circular bore as developed by O. E. Meyer[2] is

$$\eta = \frac{\pi g d r^4}{16 L V} \frac{P^2 - p^2}{P} t, \qquad (1)$$

where d = density of mercury at 0° C.

[1] F. G. Reynolds, PHYS. REV., 19, 1904.

[2] O. E. Meyer, Kinetische Theorie der Gase, 1899.

g = acceleration due to gravity.
r = radius of the capillary in cm.
L = length of the capillary in cm.
P = pressure on entering the capillary.
p = height of barometer, *i. e.*, the pressure at 0° C. at exit.
y = time in secs.
V = volume of gas transpired.

This is the expression usually made use of. Now in case of a tube of elliptical bore the formula developed by Émile Mathieu[1] is

$$\eta = \frac{\pi dg}{8LV}\frac{a^3b^3}{a^2+b^2}\frac{P^2-p^2}{P}t, \qquad (2)$$

where a and b are the semi-major and semi-minor axes respectively. Now for two tubes one with circular and the other with elliptical bore through which the same volume of gas was transpired and which had the same rate of shear, the areas of cross section would be the same; *i. e.*,

$$r^2 = ab. \qquad (3)$$

No. (1) is greater than (2) if

$$\frac{r^4}{2} > \frac{a^3b^3}{a^2b^2},$$

or by (3) if

$$\frac{a^2+b^2}{2} > \frac{a^3b^3}{a^2b^2},$$

then

$$a^2+b^2 > 2ab,$$

$$(a-b)^2 > 0,$$

and therefore the square of the difference between the semi-major and the semi-minor axes is a measure of the error introduced.

If a tube with an elliptical bore is used and the calculation is made for a tube with a spherical bore of the same cross section the result will be too high. This is illustrated in the results of experiments with a tube of circular bore and a tube of elliptical bore carried out by F. M. Pedersen.[2]

2. The difference in the form of the lines of shears at the entrance and exit of the capillary from the form of these lines in the body of the capillary. This source of error may be eliminated by using different lengths of the same tube but the plan has not been generally used.

3. There is considerable uncertainty in measuring the bore of the tube and when it is not uniform, which usually obtains, in reducing the bore to its proper value.

[1] Émile Mathieu, Comptes Rendus, 1863, Tome 57, p. 320.
[2] F. M. Pedersen, PHYS. REV., October, 1907, pp. 225–254.

4. On account of the smallness of the bore, in the case of metal tubes at least, one cannot be certain that the action of the gas on the wall of the tube does not affect the result.

5. The possibility of distortion of the lines of shear in the body of the tube because of eddies or turbulence is inherent in the capillary tube method.

The effect of all these errors is to give an apparent value of η higher than the actual value. On this account therefore it is probable that the lower values which have been obtained by the capillary tube method are closer to the correct value particularly since there is close agreement among several experimenters whose work was carried out under conditions that were considerably different.

II. *The Damping of the Oscillations of a Suspended Body.*

There are two modifications of this method.

(*a*) A spherical or cylindrical bob attached to a fine suspension has been used as a simple pendulum.

(*b*) The damping of torsional vibrations of spheres and cylinders has been used; in some cases these bodies vibrated in free air and in other cases adjacent to or confined in similar bodies. This was the method used by Tomlinson, Hogg and Reynolds. The formulæ which have been derived to connect the coefficient of viscosity and the damping of the oscillations is approximate and it is difficult to calculate or determine experimentally the allowance that must be made for the suspending parts, or the inner part and edge of the suspended body. The agreement of the results obtained by Tomlinson and Hogg seems to show that they have been very successful in estimating these factors and does much to justify the theories giving rise to the mathematical development of the formulæ which have been used. A criticism of Reynolds's work is given by Hogg in an endeavor to account for the somewhat higher value which was obtained by the former.

Summary.

1. The value of η for air has been determined for a temperature of 20.2° C. to be $1{,}812 \times 10^7$ with a probable error less than .2 per cent.

2. The variation of η with temperature has been found to agree fairly well with the relationship found by S. W. Holman and other experimenters.

3. The presence of water vapor in the air up to 60 per cent. saturation at 20° C. has no effect on η and at saturation the effect is an increase not greater than .3 per cent.

4. The method which has been used for an absolute determination of η for air at normal temperature has been shown to be exceptionally reliable.

In conclusion I desire to acknowledge my indebtedness to Professor A. A. Michelson and the Department of Physics of the University of Chicago for placing at my disposal the facilities necessary for this research, to Professor R. A. Millikan, who suggested the problem and under whose direction the work was done; to Mr. Wm. Gaertner for the loan of the clock-driving apparatus and to the University of Toronto for providing some of the incidental expenses connected with the completion of the work.[1]

[1] A fairly full list of references to the work on the viscosity of gases to 1904 is given by F. G. Reynolds, PHYS. REV., Vol. XVIII., 1904, pp. 427–431, and by F. M. Pederson, PHYS. REV., Vol. 25, 1907, pp. 249–254.

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DETERMINATION OF THE HEAT OF SOLUTION OF METALS BY MEANS OF A VACUUM FLASK CALORIMETER.

By E. E. Somermeier.

THE reliability of the results obtained in calorimetric work depends essentially upon the skill of the operator, the conditions under which the experiments are conducted, the precision with which the apparatus is calibrated, and the accuracy with which correction constants can be determined. A great deal therefore depends upon the reliability of the balance and weights, the thermometers, the radiation correction, and the water equivalent of the calorimeter.

Balance and Weights.—The analytical balances and weights usually available in a well-equipped laboratory, if properly adjusted, are entirely adequate to the requirements of the calorimeter operator, and the errors of weighing are much smaller than some of the other unavoidable errors of the determination.

Thermometers.—Thermometers graduated to 1/50° and 1/100° are obtainable without difficulty, and it is quite possible to have such instruments calibrated by the Bureau of Standards or by other authorities to 0.002°. The operator can himself determine the graduation errors by means of divided threads, and in experiments in which a high degree of accuracy is to be attained this is very desirable.

The operator must assume that the values given by the Bureau of Standards or the Reichsanstalt for the upper and lower readings of the thermometer are correct. The difference between these readings, divided by the number of degrees included between them, gives the true value for one degree. The determination of the true value of the zero mark of the thermometer (when this is needed) should be made by the usual method of determining the zero point, namely, by surrounding the bulb and stem of the instrument with closely packed, crushed ice, moistened with distilled water. Many thermometers designed for calorimetric work do not have a zero reading, but are graduated only through the working range, as for example, from 15° to 20°. In this case, if it is necessary to know the true reading for the 15° mark, an auxiliary thermometer, graduated from zero to as high as 15°, is required. The two thermometers are immersed in water at 15° and the relation of the two 15° marks is read by means of a telescope, a series of readings

for each instrument being taken. The two bulbs should be very close together, the stem should be tapped between readings, the water kept well stirred, and the temperature of the room in which the work is done should, if possible, be very close to that of the water; otherwise radiation changes are likely to be so large that high accuracy in results is rendered doubtful.

For comparison of thermometers the author has recently used a 500-c.c. Dewar flask for holding the water. The two thermometers are inserted through a stopper into the flask, and as many readings as may be desired can be taken at any temperature. The flask should be inverted between readings to insure a uniform temperature, and corrections should be made in each case for the mercury thread outside of the flask, the magnitude of the correction being proportional to the length of the thread. The changes in temperature of the water in the flask are so slow that as many readings as may be desired may be taken at any temperature The average of a series of readings is taken as the true reading at a given temperature. Violent shaking of the flask is to be avoided as the extra strain may cause the flask to collapse with the possibility of disastrous results to the thermometer. As an added precaution the flask should be covered with cloth or metal to protect the experimenter in case of possible accident.

Radiation Correction.—Accuracy in correction for radiation depends upon the particular apparatus employed, the conditions attending the experiment, and the method of correction adopted. In bomb calorimeters where the actual time of combustion is very short (only a few seconds), the error involved in the radiation correction is probably not greater than 5 or 10 calories, if the conditions for making the determination are favorable. With unfavorable conditions the error may be considerably in excess of these values. In other types of calorimetric measurements, where the reaction period is from 15 to 30 minutes, as in the solution of a metal in an acid, using an ordinary form of jacket calorimeter, the corrections may be so large that high accuracy is difficult to attain, and the values for the corrections become uncertain. Richards and Burgess endeavor to eliminate radiation entirely in their adiabatic calorimeter,[1] and their values for the heat of solution of zinc, magnesium, aluminium, iron and cadmium apparently should be very accurate. The adiabatic calorimeter is, however, very elaborate, expensive, and slow in operation, and it occurred to the author that a Dewar flask, in which radiation and conduction are reduced to so small an amount that the correction is a minor one, should be very efficient for this kind of work.

[1] Jr. Am. Chem. Soc., Vol. 22, p. 431.

The following table gives the variations in the rate of radiation and conduction for the particular 2,000-c.c. vacuum flask used as obtained from about one dozen tests ranging in time from 24 to 130 minutes and with a difference between the interior of the flask and the room temperature of from − 6 to + 9° and with an average water equivalent for the series of about 1,700 calories for each degree change in temperature.

Temperature Difference.	Average Loss in Calories per Minute.
8	1.05
7	.88
6	.72
5	.56
4	.43
3	.30
2	.19
1	.09

During shorter periods of time the observed gains or losses were occasionally several times as large as the rate shown above due to several reasons:

1. The accuracy with which the thermometer can be read is certainly not greater than ± .001° and occasionally the error may be ± .002° and for short periods of time when the observed temperature change is only .002° or .003° the possible reading error is a very large percentage of the total observed change.

2. The rate of conduction of heat from the neck of the flask into the solution or from the solution into the neck of the flask with a considerable initial temperature difference between the two is larger during a short period of observation (10 to 15 minutes) than during a longer period (30 to 60 minutes) as the two tend to reach a condition approaching equilibrium and the longer the period the more nearly the condition of equilibrium is approached.

In an actual determination when the radiation and conduction corrections are based on comparatively short periods of time (15 to 30 minutes) this larger effect of conduction enters into the actual radiation-conduction correction. But aside from making this correction larger it does not necessarily make the correction any less exact. The actual temperature change in degrees for a given determination is shown by the typical determination given later in this paper.

The idea of the use of a Dewar flask for calorimeter work is not new. Ostwald and Luther in Physiko-Chemischer Messungen call attention to its possibilities and Bogorodskii[1] in an article published since the writer

[1] J. Russ., Phys. Chem. Soc., 43, 12628.

performed his experiments used a Dewar flask for the determination of the heat of solution of Na_2HPO_4.

The experiments shortly to be described on the heat of solution of some of the metals in acid were undertaken by the author primarily to obtain more data as to the adaptability of the vacuum flask to such work, rather than with the object of obtaining any new values.

Water Equivalent.—The fourth essential for accuracy in calorimetric work is a correct water equivalent of the calorimeter, and if a Dewar flask is to be employed its water equivalent under working conditions must be determined. The author accomplished this with very satisfactory results by the addition of hot and cold water to the flask. The values used for the thermal capacity of water at different temperatures are those of Barnes as tabulated by Loeb.[1]

A 2-liter Dewar flask was used as the calorimeter, and in the determination of its water equivalent the method of procedure and the apparatus employed were as follows: The thermometer in the calorimeter flask read from 15° to 25° and was graduated in 1/100°. The graduation errors of this thermometer were determined by the author by means of divided threads. About 50 separate points were determined and a curve of intermediate positions was plotted. This calibration is accurate to within ± 0.002° and for most readings to within ± 0.001°. The Reichsanstalt certificate for this thermometer gives readings to 0.01° for each whole degree, and these values in all cases coincided with the curve obtained by divided threads. The true value for a degree on this thermometer, computed from the Reichsanstalt value for 15° and 25°, is 1.002°. Comparison of the readings on this thermometer with those on a thermometer calibrated by the Bureau of Standards confirm this value to within 0.001°. The two thermometers, used in measuring the temperature of the hot and cold water, were graduated to 0.005°, and the graduation covered ranges of from 0° to 26° and from 24° to 50°. Each was calibrated by the Reichsanstalt for the true value of the degrees. The relation of the readings on each of the three thermometers to the true zero point was ascertained by the author by determining the value of the zero point of the one reading from 0° to 26° and comparing the readings on this thermometer with points on the other two.

The hot or cold water to be added to the calorimeter was kept in a 500 c.c. vacuum flask provided with a cork stopper through which was inserted a long glass tube extending nearly to the bottom of the flask (for admitting air while emptying the flask), and a short sleeve of test tubing, 2 cm. long, through which the thermometer was introduced

[1] Ind. and Eng. Chem., Vol. 3, p. 175.

when temperature readings were being taken, and by means of which the flask was emptied into the calorimeter. The flask serving as calorimeter was provided with a three-hole cork stopper. Through one hole the thermometer was inserted; through another was fitted a short piece of thin test tube, 2 cm. in length and of sufficient diameter to permit the ready introduction of the emptying tube with which the small flask was provided. The third hold in the stopper served merely to permit the escape of air while pouring the hot or cold water into the flask, and at other times was kept loosely stoppered, as was also the larger opening.

In making a determination of the water equivalent, about 1,200 grams of water at any convenient temperature was weighed in the large calorimeter flask, the stopper adjusted, and the thermometer slipped into such a position that the bulb was entirely immersed. About 450 grams of water, approximately 20° hotter (or colder) than the water in the calorimeter flask, was weighed into the smaller flask, the stopper tightly inserted, and the thermometer slipped into place, being held in the glass sleeve by a short piece of close-fitting rubber tubing. A series of readings was then taken on each thermometer, the large flask being shaken by a rotary motion between each reading, and the small flask being completely inverted. The readings on the thermometer in the calorimeter were made through a telescope, while those on the thermometer in the hot (or cold) water flask were made with a reading lens such as is used with a Junker calorimeter.

When a satisfactory series of readings had been obtained, the thermometer was slipped out of the small flask and its contents quickly poured into the larger one, care being taken to properly insert the delivery tube of the small flask into the receiving tube of the calorimeter. The time required for the process was about four seconds. The weight of glass tubing heated (or cooled) in adding the water was only 1.6 grams, or for a difference of temperature of 15° the correction is about 4.8 calories. Experiments on the heat radiation of water from tubes of the same size gave a radiation loss in four seconds, and for a temperature difference equal to that used in the experiment, of only 1 calorie. As the larger portion of the four seconds during which water is poured into the flask is doubtless required to heat (or cool) the tubing, the actual radiation gain (or loss) is practically negligible. The heat carried off by the escaping air when cold water is added, or gained when hot water is added, amounts to less than 1 calorie and does not require correction.

From the temperature and weight of water in the calorimeter, and the temperature and weight of the water added, together with the ob-

served changes in temperature, the following values were obtained for the water equivalent of the calorimeter flask:

Adding hot water:	38.2	35.0				
Adding cold water:	37.9	36.8	37.0	35.6	33.8	35.6

The average value, 36.2, was taken as the water equivalent of the flask and thermometer.

As a check on this value it is possible to calculate the water equivalent in the following way. The water equivalent of the portion of the thermometer in the flask was 4.2 calories. The weight of the calorimeter flask was 555 grams. Allowing 75 grams for the upper portion of the neck leaves 480 grams of the weight of the outer and inner flasks. Assuming the outer flask to weigh twice as much as the inner, gives 160 grams as the weight of the inner flask. Multiplying this weight by 0.2 (the specific heat of glass) gives 32 calories, which, added to the water equivalent of the thermometer, gives a calculated value of 36.2 calories as the water equivalent of the apparatus—in very close agreement with the experimental value.

With an average rise (or fall) of about 5° in the water in the calorimeter, and a fall (or rise) of about 15° in the water added, and with about 1,650 grams of water in the calorimeter at the conclusion of the experiment, the probable errors of a single determination are of about the following magnitude:

	Calories.
Error in weight of water added (± 0.3 gram)	± 4.5
Error in weight of water in calorimeter (± 0.2 gram)	± 1.0
Error in transferring correction (calculated)	± 5.0
Error in initial reading (calorimeter thermometer), ± 0.002°	± 2.5
Error in final reading (calorimeter thermometer), ± 0.002°	± 3.4
Error in reading hot (or cold) thermometer, ± 0.005°	± 2.2
Stem correction (calorimeter thermometer), ± 0.001°	± 1.6
Stem correction (hot or cold water thermometer), ± 0.001°	± 0.5
Error in radiation correction, ± 0.002°	± 3.2
Total	± 23.9

If all of these errors should have the same sign, the error in the water equivalent for a single determination would be 23.9 divided by 5, or 4.8 calories. But with the chances of some of the errors being of opposite signs, the probable error in a single determination should not exceed 10 calories, giving a value of 2 calories for the error in the water equivalent. Inspection of the values obtained for the water equivalent shows 6 out of 8 of them to fall within this limit.

The magnitude of the constant errors of a determination is about as follows:

	Calories.
Error in calibration of calorimeter thermometer, ± 0.002°	± 3.4
Error in calibration of hot (or cold) water thermometer, ± 0.005°	± 2.2
Error in adjustment of the two thermometers, ± 0.01°	± 4.5
Error in specific heat of water, probably less than	± 2.0
Total	± 12.1

If all of these errors should have the same sign, the maximum constant error in the water equivalent would be 12.1 calories divided by 5, or ± 2.4 calories. But the chances that some of the error are of opposite signs are about 7 to 1; so the probable error is not greater than ± 1 calorie. Taking into account the combined magnitude of variable and constant errors, the value 36 calories obtained for the water equivalent should be accurate to within less than ± 2 calories.

Heat of Fusion of Ice.—As a preliminary test of the possibilities of the calorimeter, some experiments were made on the heat of fusion of ice. The mode of procedure was to add weighed quantities of ice at 0° to weighed quantities of water in the calorimeter at a convenient observed temperature, and determine the fall in temperature of the water. From these data, together with the water equivalent of the calorimeter, the heat of fusion is readily calculated. Three determinations gave values as follows: 79.98, 79.88, 79.89, or an average of 79.92, which agrees almost exactly with Smith's value for the same constant.[1] These results are regarded as tentative, however, as it was later found that the ice sticks added may have been moist instead of dry. The results of experiments on this point have been described in detail elsewhere.[2]

Heat of Solution of Metals in Acid.—The manipulation involved in determining the heat of solution of a metal in an acid is very simple. A convenient quantity of acid of the desired strength is weighed in the vacuum calorimeter, the temperature of the acid being adjusted before it is put into the flask. The stopper and thermometer are inserted and readings are taken with a telescope at intervals of from 3 to 5 minutes, until a satisfactory series is obtained. The flask is shaken and the thermometer tapped between readings. A weighed quantity of the metal is then poured into the flask through the test-tube sleeve, which is again loosely stoppered. The flask is shaken from time to time and readings are taken at intervals of from 5 to 10 minutes, until they indicate complete solution of the metal, and a regular rate of gain or loss is established. The heat evolved is then calculated from the data obtained.

The temperature range during determinations was between 16.3° and 21.5°, which is very nearly the same range chosen by Richards and

[1] PHYS. REV., Vol. 17, p. 193, Oct., 1903.
[2] PHYS. REV., Vol. 35, p. 128, Aug., 1912.

Burgess. The ratio of acid to metal was in all cases practically the same as in their experiments. By actual weight, about two thirds more of each was used, these quantities being better adapted to the size of the vacuum flask calorimeter. The three metals selected were zinc, aluminium and magnesium.

The temperature observations obtained during a determination of the heat of solution of magnesium in dilute hydrochloric acid are as follows:

Time.	Temperature.	Room Temperature.	Difference between Temperature of Flask and Room Temperature.
4:40	16.300	——	——
4:43	16.301	——	——
4:45	16.302	19.8	——
4:50	16.307	——	——
4:53	16.309	——	——
4:56	16.311	——	−3.5
Zinc added			
4:60	17.400	——	−2.3
5:04	19.150	——	−0.4
5:08	20.300	19.6	+0.7
5:12	20.530	——	+1.1
5:16	20.556	19.4	+1.1
5:20	20.572	——	+1.1
5:25	20.588	——	+1.2
5:30	20.587	19.4	——
5:33	20.586	——	+1.6
5:55	20.583	19.0	——
6:15	20.581	18.8	+1.8

The temperature 20.588 at the time 5:25 was taken as the final temperature of solution. The radiation and conduction corrections during the first ten minutes of the solution period practically balance those of the last 19 minutes as may be seen from the column of differences, the average of the first ten minutes, 4:56 to 5:06, being about − 1.9, the average of the last 19 minutes, 5:06 to 5:25 being about + 1.1. The average rate of gain per minute before the addition of the zinc with a temperature difference of 3.5° is .00066°. After the solution in the zinc with a temperature difference of 1.4°, the average rate of loss per minute is .00018°. The actual radiation-conduction correction applied in this determination by the author from the above data was + .0005°, a correction amounting to only .8 of one calorie.

METALS USED.

Zinc.—The zinc was presumably of the same grade as that used by Richards and Burgess (Merck's drop-shot zinc). It was washed with

alcohol and dried before weighing. Tests as to its purity indicated the presence of 0.1 per cent. of iron. One gram of iron is equivalent to 0.79 gram of zinc in heating value when dissolved in acid; consequently for the present purposes the zinc was taken as 99.98 per cent. pure.

Magnesium.—Ribbon magnesium was selected. It was well polished and burnished before weighing by means of Tripoli powder and a piece of heavy cloth. Tests as to its purity resulted in a precipitate of iron and aluminium oxides equal to 0.1 per cent. of the magnesium, and equivalent to 0.06 per cent. of iron plus aluminium. The purity of the magnesium was therefore assumed to be 99.9 per cent.

Aluminium.—Sheet aluminium was used, being first washed with dilute hydrochloric acid and afterwards with alcohol. Tests for the presence of impurities gave 0.27 per cent. of iron, equivalent to 0.02 per cent. of aluminium; 0.16 per cent. of silicon, equivalent to 0.21 per cent. aluminium; 0.06 per cent. of carbon. The heat of evolution of the hydrocarbons is small and this carbon is assumed as having no heating value or as equivalent to 0.00 per cent. of aluminium in heating value. The total of impurities present amounted to 0.49 per cent., equivalent to 0.23 per cent. of aluminium. The purity of the aluminium was therefore assumed to be 99.75 per cent.

At the outset of the experiments it was the intention of the author to make use of acids of the same strength as those used by Richards and Burgess, namely, $HCl.20H_2O$ and $HCl.200H_2O$. In preparing the acids the preliminary standardization was made against a one tenth normal solution of sodium hydroxide which had been on hand for some time, methyl orange being used as the indicator. The final standardization, based upon the weighing of chlorine as silver chloride, was delayed until determinations of the heat of solution of each of the metals had been made. When this final standardization was made, it developed that the acid was about 4 per cent. stronger than had been intended, and investigation showed that this was due to the fact that the sodium hydroxide had acted upon the glass of the containing bottle, and had gained strength to the extent of about 4 per cent. As some determinations had been made before this fact was discovered, the series was completed with this stronger acid, but with the intention of preparing a second set of acids of exact strength and making a second series of measurements. A new solution of hydrochloric acid of the strength $HCl.20H_2O$ was actually prepared, and two determinations of the heat of solution of aluminium were completed, when the calorimeter flask went to pieces and ended the experiments until it is possible to secure and standardize another flask. Meanwhile it seems advisable to publish the results so far obtained.

In the calculation of the results, Richards's values for specific heats were taken as a basis, and the following values were used:

Specific heat, $HCl.20H_2O$ = 0.8486 (Richards).
" " $HCl.19.15H_2O$ = 0.8420 (Interpolated).
" " $HCl.200H_2O$ = 0.9814 (Richards).
" " $HCl.191.5H_2O$ = 0.9806 (Interpolated).

The temperature range through which Richards and Burgess worked was from 16° to 20°, while that employed by the author was from 16.5° to 21°. This slight difference can cause very little change in the specific heats, and the error in the assumed specific heats based on Richards's values cannot be large enough to materially affect any of the results.

The correction for the evolution of hydrogen was 213 calories for each gram molecular volume, which is practically the value adopted by Richards. The correction for the heat absorbed by the added metal was obtained by multiplying the weight of the metal by its specific heat, and by the difference between the final temperature of the solution and the temperature of the room at the time of the addition of the metal. The specific heats adopted were as follows: zinc = 0.098; aluminium = 0.202; magnesium = 0.245.

In determining the heat of solution of aluminium, the reaction between the metal and the acid was accelerated by the addition of a few drops of a solution of chloro-platinic acid to the hydrochloric acid solution. The heat evolved by the liberation of the platinum was calculated from the weight of the platinum precipitated, making use of the same data employed by Richards.

The atomic weights used were as follows: zinc, 65.37; magnesium, 24.32; aluminium, 27.10. All weighings of acid and metals were corrected to vacuum conditions.

The values obtained are those of the heat of solution of zinc in $HCl.19.15H_2O$; of magnesium in $HCl.191.5H_2O$; of aluminium in $HCl.19.15H_2O$; and in $HCl.20H_2O$. The data for these values are as follows:

From data given by Richards, Rowe and Burgess,[1] the heat of dilution of zinc in $HCl.20H_2O$ to zinc in solution in $HCl.200H_2O$ is 6,400 calories. The heat of dilution of zinc in $HCl.19.15H_2O$ to zinc in $HCl.200H_2O$ will evidently be greater than this—probably by as much as several hundred calories. 250 calories may be assumed as a conservative value. The dilution of the solution of magnesium in $HCl.191.5H_2O$ to magnesium in $HCl.200H_2O$ is probably attended with very little thermal change, and the value obtained for solution in $HCl.191.5H_2O$ is therefore prac-

[1] Jour. Am. Chem. Soc., Vol. 32, p. 1185.

No.	Metal.	Grams Taken.	Grams Acid.	Temperature Rise.	Water Equivalent of Acid + 36 for Calorimeter.	Calories of Heat Developed.	Correction for Platinum.	Heat Absorbed by Metal Added.	Correction for Hydrogen.	Heat per Gram Atomic Weight of Metal.	Heat per Gram Atomic Weight Corrected to 100 Per Cent. Purity.
1	Zinc.....	13.0758	1641(*a*)	4.2620	1417.7	6042.2	00	0.0	+42.6	30403	
2	Zinc.....	13.0756	1641(*a*)	4.2634	1417.7	6044.2	00	+3.8	+42.6	30434	
3	Zinc.....	13.0762	1641(*a*)	4.2633	1417.7	6044.1	00	+6.2	+42.6	30439	
	Average.....									30425	30430
4	Magnesium.....	1.6225	1726(*b*)	4.2866	1728.5	7409.4	00	+1.3	+14.2	111310	
5	Magnesium.....	1.6227	1726(*b*)	4.2866	1728.5	7409.4	00	+0.3	+14.2	111294	
6	Magnesium.....	1.6225	1726(*b*)	4.2870	1728.5	7410.1	00	+0.3	+14.2	111306	
	Average.....									111303	111410
7	Aluminum.....	1.3554	1721(*a*)	4.2910	1485.1	6372.6	−0.4	0.0	+16.0	127802	
8	Aluminum.....	1.3555	1721(*a*)	4.287	1485.1	6366.7	−0.4	0.0	+16.0	127693	
9	Aluminum.....	1.3553	1721(*a*)	4.288	1485.1	6368.1	−0.4	+0.4	+16.0	127705	
10	Aluminum.....	1.3552	1721(*a*)	4.290	1485.1	6371.1	−0.4	0.0	+16.0	127752	
	Average.....									127738	128060
11	Aluminum.....	1.3555	1707(*c*)	4.3038	1484.6	6389.4	−0.4	0.0	+16.0	128053	
12	Aluminum.....	1.3555	1707(*c*)	4.3034	1484.6	6388.8	−0.4	0.0	+16.0	128043	
	Average.....									128048	128360

a = 19.15 H_2O, HCl. *b* = 191.5 H_2O, HCl. *c* = 20 H_2O, HCl.

tically the same as for solution in $HCl.200H_2O$. The following table gives a comparison of the values obtained by the author with those obtained by Richards:

	Author.		Richards.	
	Solution in $HCl.19.15H_2O$.	Solution in $HCl.20H_2O$.	Solution in $HCl.20H_2O$.	Difference.
Zinc	30,430	(30,680)	30,180	400
Aluminium	128,060	128,360	126,000	2,360
	Solution in $HCl.191.5H_2O$.	Solution in $HCl.200H_2O$.	Solution in $HCl.200H_2O$.	
Magnesium	111,410	(111,410)	110,150	1,260

The values for zinc and magnesium which are included in parentheses are based upon experiment together with data already given.

In making the determinations the author used one fifth of a gram-atom of zinc; one fifteenth of a gram-atom of magnesium; and one twentieth of a gram-atom of aluminium. With these weights, the differences tabulated above, computed to a single determination, are as follows: zinc, 80 calories; aluminium, 118 calories; magnesium, 84 calories. In the case of aluminium a fraction of this discrepancy may be due to an actual difference in the materials used, and the corrections applied for the impurities in the metal. A small fraction of the discrepancy in the case of zinc and magnesium may also be due to the same causes. It does not seem possible, however, that any large fraction of the discrepancies can be accounted for in this way.

In regard to errors in a determination which might be attributed to the apparatus, it may be said that all of the apparatus used by the author was checked at every point. The corrections to the thermometers have already been described. The weights were all adjusted very carefully to one another, and to a standard set secured through Troemner, and double checked by him against standards supplied by the Bureau of Standards. Errors in the thermometers or weights cannot, therefore, have been of any appreciable magnitude. The error in the water equivalent of the calorimeter is believed to have been safely within ± 2, which amounts to less than 10 calories in a determination. The errors in reading the thermometers amount to only 1.6 calories for each 0.001°, so that these cannot account for any great difference in results. The total radiation corrections in most cases amounted to less than 5 calories and in no case to more than 10, and it does not seem possible that such errors are accountable for any appreciable fraction of the discrepancy.

The heat obtained during a determination must have come from the reaction as no complicated stirring apparatus was used, and experiments showed that the heat produced by shaking the solution during a deter-

mination amounted to less than 3 calories; moreover, the greater part of this error is eliminated in the initial and final rate correction.

In reviewing the work of Richards and Burgess the author notes the fact that the water equivalent of the adiabatic calorimeter, used in the solution of the metals in acid, is calculated and is not verified by experimental determinations. As to whether the use of a calculated water equivalent, not verified by experimental means, accounts for any of the discrepancy in results, the author is unable to venture an opinion.

In the opinion of the author it is entirely possible that the radiation correction for the adiabatic calorimeter, instead of being zero, may have an actual value; and that for the same operator, the same calorimeter, and the same set of conditions, it may be practically a constant. Such a constant, if it really exists, would, in the case of a calorimeter with a calculated water equivalent, cause the results to be uniformly low or high; whereas in the adiabatic bomb calorimeter used by Richards and Jesse,[1] in measuring the heat of combustion of octanes, etc., the water equivalent is experimentally determined against cane sugar. Any systematic error is absorbed in this experimentally determined water equivalent, and is eliminated from the final results. So far as the author is aware there are no published data giving comparisons between calculated and experimental water equivalents for an adiabatic type of calorimeter, and as to whether or not they agree, he has at present no means of knowing.

The results described in this paper are to be regarded as preliminary only, and the author hopes to find time and opportunity for continuing the investigation. Meanwhile he hopes that the publication of the results already secured may stimulate other investigators to take up thermal measurements.

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[1] Jour. Am. Chem. Soc., Vol. 32, p. 268.

THE ELECTRON THEORY OF PHOSPHORESCENCE.[1]

BY CHESTER A. BUTMAN.

IT is the purpose of any theory of phosphorescence to explain the mechanism of the secondary phenomena which causes the luminosity to continue after the exciting light is shut off.

The theory proposed is that the incident light causes the electrons in the light-emitting atom of the complex phosphorescent molecule to be brought to a critical-energy-content causing the selective emissions characteristic of the substance; at the same time the light causes electrons to be ejected from the photoelectric atom; the return of the electrons to the molecule by collision causes the luminosity to continue.

The following is a list of most of the facts that any theory of phosphorescence must explain.

1. Luminosity after the exciting light is cut off.
2. Relation to Stokes' law.
3. Rate of phosphorescent decay.
4. The extinguishing action of red light.
5. The flashing up caused by heating.
6. Why a band spectrum is produced.
7. How two bands with different rates of decay can exist in the same material.
8. Why the generation-distribution curves of Lenard and Klatt are possible.
9. Relation to thermoluminescence.
10. Relation of triboluminescence.
11. Relation to gas phosphorescence.
12. Relation to the general production of luminosity.
13. Relation of the color of the material to the color of the bands.
14. Relation of the intensity of the phosphorescence to the intensity of the exciting source.
15. Why a maximum phosphorescent intensity exists.
16. Why a certain time is necessary to produce the duration bands.
17. Why infra-red phosphorescence can exist.

[1] See also abstract of paper read before the American Physical Society, March 2, 1912; PHYS. REV., Vol. 34, p. 316, 1912.

18. Shift of the bands when exposed to long waves.
19. Relation to the absorption of light.
20. Why the brightening up is more prominent at low temperatures than the decay when exposed to red light.
21. Relation to fluorescence.
22. Excitation by alpha particles.
23. Excitation by beta particles.
24. Excitation by canal rays.
25. Excitation by Röntgen rays.
26. Relation of phosphorescent intensity to the amount of light-producing metal present.
27. Effect of the flux on the intensity.
28. Relation to the dielectric constant.
29. Why the alkaline earths and zinc occur so prominently in phosphorescent compounds rather than other elements.
30. Why sulphur is usually present in long duration phosphorescent compounds.
31. How it is possible to substitute selenium for sulphur and have a phosphorescent compound.
32. Relation to the photoelectric effect.
33. Relation to photoelectric fatigue and recovery.
34. Relation to the actinodielectric effect.
35. Relation between phosphorescent inorganic and organic bodies.
36. Relation to temperature changes.
37. Why phosphorescence is a property of the solid state.

The theory outlined here differs from that of Lenard in several particulars. In the case of the alkaline earth sulphides the photoelectric atom is held to be sulphur, while Lenard's theory indicates that it is the heavy metal. Recent experiments seem to support the view taken here. For instance, it has been shown by Pohl and Pringsheim[1] that the photoelectric effect of Bi stops at about 3,100 Ang. This means that Bi would not be photoelectrically active if the light had first passed through glass. Again Pohl and Pringsheim[2] have shown that when two photoelectric components are in combination that the combination is not excited by wave-lengths shorter than will excite either component not in combination. Hence it does not seem probable that in the phosphorescent combination Ca-S-Bi that the Bi is photoelectrically active after the light has passed through glass. Nevertheless Ca-S-Bi is strongly phosphorescent and gives a photoelectric effect with light that has passed

[1] R. Pohl and P. Pringsheim, Verh. d. D. Phys. Ges., 13, p. 480, 1911.
[2] R. Pohl and P. Pringsheim, Verh. d. D. Phys. Ges., 12, pp. 215–228, 349–360, 1912.

through glass. However, it has been shown by the author[1] that sulphur is photoelectric with light through glass. It has been shown by Lenard and Saeland,[2] and confirmed by the author,[3] that those rays which cause Ca-S-Bi to phosphoresce, cause it to be photoelectric. Also those rays which do not cause it to phosphoresce do not give a photoelectric effect. Hence, it would seem that it is necessary to have a photoelectric component in order to have a phosphorescent compound. This last being the case, it is seen why it is that sulphur appears so prominently in phosphorescent compounds of long duration. The function of the sulphur then is to supply a photoelectric component having high insulating properties. It is necessary that phosphorescent substances should be good insulators so that the charges will recombine slowly, making a phosphorescent compound of long duration.

Another fact which supports the theory that sulphur is responsible for the electrical behavior of the alkaline earth sulphides, is that sulphur is actinodielectric, as has been shown by the author.[4] It was discovered by Lenard and Saeland,[5] and the work extended by Oeder, Ramsauer and Hausser,[6] that Ca-S-Bi was actinodielectric. It was shown that if Ca-S-Bi be placed between a net and a plate (the plate being connected to an electrometer, the net to a source of potential) that if the substance was exposed to light a deflection of the electrometer would take place. This effect differs from the photoelectric effect in that the deflection takes place in the direction of the applied field, whereas the photoelectric effect goes in one direction. Another difference is that Ca-S-Bi gives no photoelectric effect with red light but does give an actinodielectric effect with it. It was shown by the author[7] that sulphur gave an actinodielectric effect with red light.

Another confirmation of the theory would seem to be found in the case of quinine sulphate. Miss Gates[8] found that this substance was phosphorescent while cooling after heating to about 100° C. She also found that the radiations from this substance ionized the air better with a *positive* field than a negative. It would seem, then, that the heating sets some of the electrons free from the sulphur so that the same condi-

[1] C. A. Butman, Amer. Jour. Sci., Vol. 34, pp. 133–139, 1912. "The Photoelectric Effect of Phosphorescent Material," also PHYS. REV., Vol. 34, p. 158, 1912.

[2] P. Lenard and Sem. Saeland, Ann. der Phys., Vol. 27, pp. 476–502, 1909.

[3] C. A. Butman, Amer. Jour. Sci., Vol. 34, pp. 133–139, 1912.

[4] C. A. Butman, Amer. Jour. Sci., Vol. 34, p. 139, 1912.

[5] Loc. cit.

[6] Rob. Oeder, C. Ramsauer, W. Hausser, Ann. der Phys., pp. 445–454, 1911.

[7] C. A. Butman, Amer. Jour. Sci., Vol. 34, pp. 133–139, 1912.

[8] J. J. Thomson, "Conduction through Gases," p. 425.

tion obtains as that of the alkaline earth sulphides after having been exposed to light.

Again it is stated by Lenard[1] and confirmed by the author, that it is impossible to make a phosphorescent compound out of such elements as Ca and Bi without sulphur. However, it may be predicted from the theory that if a photoelectric component with good insulating properties, giving a photoelectric effect through glass could be found, it could be substituted in place of sulphur and a phosphorescent compound formed. This prediction would seem to be fulfilled in the recent work of Pauli[2] who has made a phosphorescent compound by substituting selenium for sulphur.

MECHANISM OF LIGHT PRODUCTION.

The rate of decay of the phosphorescent light would seem to indicate that the phenomenon was a kinetic phenomenon. The rate of decay of Sidot blende has been studied in great detail by Nichols and Merritt.[3] Practically no change is necessary in the considerations advanced by them to show that a recombination of the electrons by collision, as proposed here, would give the laws of decay.

According to this theory, the flashing up of the substance when exposed to heat can be attributed to increasing the rate of collision.

The phenomena of the photoelectric fatigue and recovery worked upon by the author[4] are best understood by assuming that the electrons set free get entangled in the substance and build up fields in it. "Fatigue would then be due to this accumulated field building up." "Recovery would seem to be due to the recombination of the electrons, which probably takes place quite slowly." The foregoing seems to offer an explanation of why a certain time is necessary to produce the duration bands. For it would seem that it would be necessary to set free a large number of electrons before luminosity would follow on their recombination. It also seems to show why a maximum phosphorescent intensity exists, as the rate of recombination would not probably exceed a given value.

That luminosity can be maintained by the recombination of the electrons would seem to be well supported from the phenomena of gas phosphorescence. The theory can be applied with success to the experiments by C. C. Trowbridge[5] on gas phosphorescence. He found that it took

[1] P. Lenard, Ann. der Phys., 31, p. 668, 1910.

[2] W. E. Pauli, Ann. der Phys., 38 (4), pp. 870–880, 1912.

[3] Nichols and Merritt, PHYS. REV., 27, p. 367, 1908.

[4] C. A. Butman, Amer. Jour. Sci., Vol. 34, pp. 135–139, 1912.

[5] C. C. Trowbridge, PHYS. REV., Vol. 32, pp. 129–151, 1911.

some time to form the phosphorescence (that is, for the gas to get into the proper electrical condition).

Another fact found was that "The intensity of luminosity of the phosphorescing gas depended in a marked manner on the pressure of the gas, and that the intensity was very much less when the gas pressure was low than when it was high." This last would seem to be explained as being due to the rate of recombination being more rapid at a higher pressure.

The theory would indicate that the rate of decay of the phosphorescence would vary according to the electrical conditions of the gas. This is seen to be the case from the fact that "The rate of decay may vary considerably while the gas pressure remains constant." However, one would expect that the rate of decay would depend somewhat on the pressure and it was found that there was a given pressure which gave the longest decay. Nevertheless, as the theory would indicate, the phosphorescence was not as bright as at higher pressures. He says further: "There is also a hysteresis effect which makes the behavior of the phosphorescence depend on the previous history of the gas, although the electrodeless discharge itself appears to suffer no alteration." This seems to be the same as the hysteresis effects observed in solid phosphorescent substances. The gas molecules appear to become charged and luminosity is continued, due to the recombination of the electrons at the time of collision. As Sir J. J. Thomson[1] has already assumed, the molecules must have acquired a certain amount of energy in order that luminosity be produced.

THE CAUSE OF THE SPECTRA OF PHOSPHORESCENT MATERIAL.

The light-producing element in the phosphorescent alkaline earth sulphides is held by everybody to be mainly due to the heavy metal. However, the spectra are somewhat modified by being in combination with the alkaline earth element and the sulphur. It is the idea of the author that the light from the heavy metal is a selective emission from that element. This explains why the color of the phosphorescent light is the same as the color of the substance by reflection, also why a banded spectrum is given out and why different bands can be generated by choosing incident light of the proper frequency. As is to be expected there is a direct relation between the regions where the light is absorbed and where it is emitted. Again Stokes's law should hold in some degree. These last have been verified by Bachem[2] recently. The work of Bruninghaus[3] also supports the view taken here.

[1] J. J. Thomson, Nature, 73, pp. 495–499, 1906.

[2] Alb. Bachem, Ann. der Phys., Vol. 38, pp. 697–720, 1912.

[3] Bruninghaus, Le Radium, April, 1911.

The composition of an inorganic phosphorescent compound then is an alkaline earth metal which is transparent to the rays sent out from the heavy metal and which acts as a dilutant, a trace of a heavy metal giving a selective emission in the visible region, and a photoelectric component active near the visible region and also being a good insulator. These three elements to be in chemical combination. Only a trace of the heavy metal can be present in order that the insulating properties may not be impaired. Hence, infra-red phosphorescence is seen to be possible from the theory in that all that is necessary is to find a metal having a selective emission in the infra-red.

The changes produced by changing the temperature are hard to explain at present, but no doubt the change in the rate of collision and the mean free path changes the critical energy-content and also in some cases the period of the emitting electrons.

The extinguishing action of red light is another hard problem requiring explanation. This may be explained in the following manner. According to the theory it is necessary for the emitting electronic systems to have a certain amount of oscillating energy, in order to produce luminosity. Now the red light has a somewhat less frequency than the emitted light and it may be assumed it dampens the vibrations of the oscillating system so that they fall below their critical value and the luminosity ceases. An experiment which supports this view, is that if a phosphorescent substance be exposed to red light for a sufficient length of time it will not generate luminosity when exposed to the usual exciting sources. This may be interpreted that the red light caused the electronic systems to take up forced vibrations which were maintained for some time and that the usual exciting light could not bring the oscillations up to their critical value in a brief time. It seems quite certain that the oscillations are continued for a considerable time from the large number of interference fringes observed with light from a phosphorescent substance by Voigt.[1] Another experiment explained by this theory is the shift of the bands toward the red end of the spectrum when the phosphorescent substance is exposed to long light waves. It would appear that the long waves dampened the frequency causing the shift in the position of the band.

The foregoing discussion has dealt with the inorganic phosphorescent substances, but inasmuch as the organic substances examined by Kowalski[2] have practically the same properties as the inorganic, it would seem to hold in the case of organic substances also.

It is to be noticed that the theory outlined here gives a theory of

[1] Voigt, Arch. Neerl (2), 6, pp. 352-366, 1901.

[2] Kowalski, Phys. Zeit., 12, pp. 956–969, 1912.

fluorescence as well as phosphorescence. If the incident light causes the oscillating systems to come to their critical energy-content, and they emit light, this is a case of fluorescence. However, as soon as the exciting light was removed, the oscillating systems would fall below their critical value and cease to emit light. It would also seem from the theory that there would be no observable lag in the production of the emitted light, which appears experimentally to be the case. Many fluorescent substances are probably photoelectric, but being in the liquid state, the recombination takes place quickly. Nevertheless if these substances are brought into the solid state in the presence of an insulator, they become phosphorescent, as has been shown by Kowalski.[1]

AMHERST, MASS.,
August 14, 1912.

[1] Loc. cit.

ON THE THEORY OF RELATIVITY: MASS, FORCE AND ENERGY.

By R. D. Carmichael.

Introduction.

In a previous paper[1] I have given an analysis of the characteristic postulates on which the theory of relativity depends and have developed in a general way some of the fundamental conclusions of this theory. The plan of treatment adopted makes it possible to arrive at these results by arguments which are not complicated in form; and the notions which enter into them are of simpler character than those usually to be found in memoirs on this subject.

It seems desirable that the general theory should be further worked out along the same lines, even though this should require in part a repetition of some things already in the memoirs. Accordingly, in the present paper I develop the fundamental properties[2] of mass, force and energy, using as a basis the theorems of my previous paper. *In the derivation of these results the theory of electricity is not employed.* Consequently the conclusions are of wider applicability than when they are proved by means of electrical theory; in particular, they may be applied to the derivation of results in the theory of electricity itself.

In § 1, after giving some definitions, I state the laws of conservation of momentum and energy and electricity and the principle of least action in the form in which I shall have occasion to use them. The law of conservation of electricity is employed in this paper only in the applications of the results concerning mass and energy.

In § 2 the question of the dependence of mass on velocity is treated. First the transverse mass of a moving body is determined by the elegant method of Lewis and Tolman. The relation between transverse mass and longitudinal mass is found by the method of Bumstead, and thus the longitudinal mass of a moving body is obtained.

In § 3 dimensional equations are employed to derive the relations of acceleration and force in two systems of reference.

In § 4 from considerations concerning the mass of a moving body two essential equivalents of postulate R are determined, each of which

[1] Physical Review, Vol. 35 (1912), pp. 153–176.

[2] Several applications of the principal conclusions are also given.

furnishes a possible means for the experimental proof or disproof of the theory of relativity. The researches of Bucherer have been thought to afford the requisite experimental confirmation in the first case; this matter is treated in § 5. In § 6 suggestions are given for a new *crucial* experiment for testing the theory of relativity, this being associated with the second essential equivalent of R in § 4. The writer desires to call especial attention to this proposed experiment.

In § 7 the intimate relation of the mass and the total energy of a body is pointed out and two theoretical means are suggested for determining the velocity of light indirectly, that is, without direct measurement of this velocity. These experiments, if they could be performed with sufficient accuracy, would afford an interesting and striking confirmation of the theory of relativity, provided of course that they turn out according to the predictions of this theory.

A few remarks on the principle of least action are found in § 8, and § 9 is given to some speculative considerations which are intended as brief suggestions of means by which one may represent to himself the conclusions of relativity as natural parts of a consistent view of physical phenomena.

§ 1. Fundamental Definitions and Postulates.

If m, M and v are respectively the mass, momentum and velocity of a body we shall assume (as in the classical mechanics) that they are connected by a relation of the form

$$M = mv;$$

and hence any one of these quantities is determined in terms of the other two (except that mass is not thus determined when velocity and momentum are zero). We shall take mass and velocity to be the two fundamental quantities, so that momentum is *defined* in terms of them.

Likewise we shall define the kinetic energy E of a moving body by means of the usual relation

$$E = \int_0^v Mdv = \int_0^v mvdv.$$

Later we shall see that "mass" is variable and is not in general independent of the direction in which it is measured; consequently, we must take for m in the above formulæ the mass of the body in the direction of its motion.

We shall take for granted the following laws of conservation of momentum and energy and electricity:

POSTULATE C_1. *The sum total of momentum in any isolated system remains unaltered, whatever changes may take place in the system, provided that it is not affected by any forces from without.*

POSTULATE C_2. *The sum total of energy in any isolated system remains unaltered, whatever changes may take place in the system, provided that it is not affected by any forces from without.*

POSTULATE C_3. *The sum total of electricity in any isolated system remains unaltered, whatever changes may take place in the system, provided that the system as a whole neither receives electricity from nor gives out electricity to bodies not belonging to the system.*

The "action" of a moving body in passing from one position to another may be defined as the space integral of the momentum taken over the path of motion. If we denote this action by A we have therefore

$$A = \int M ds = \int mv ds.$$

Now $ds = vdt$, so that we have also

$$A = \int mv^2 dt.$$

If several bodies are involved we have

$$A = \Sigma \int mv ds = \Sigma \int mv^2 dt$$

where the summation is for the various bodies in the system.

We may state the fundamental principle of least action in the following form:

PRINCIPLE OF LEAST ACTION. *The free motion of a conservative system between any two given configurations has the property that the action A is a minimum, the admissible values $\bar{A}$ of the action with which A is compared being obtained from varied motions in which the total energy has the same constant value as in the actual free motion.*

§ 2. DEPENDENCE OF MASS ON VELOCITY.

Suppose that we have two systems of reference S_1 and S_2 moving with a relative velocity v. We inquire as to whether, and in what way, the mass of a body as measured on the two systems depends on v. Will a given body have the same measure of mass when that mass is estimated in units of S_1 and in units of S_2? And will the mass of a body depend on the direction of its motion by means of which that mass is measured? Our purpose in this section is to answer these two questions.

The two most important directions in which to measure the mass of a body are, first, that perpendicular to the line of relative motion of S_1 and S_2, and, secondly, that parallel to this line of motion. For convenience

in distinguishing these we shall speak of the "transverse mass" of a body as that with which we have to deal when we are concerned with the motion of the body in a direction perpendicular to the line of relative motion of S_1 and S_2; when the motion is parallel to this line we shall speak of the "longitudinal mass" of the body.

Lewis and Tolman[1] determine what they call the "mass of a body in motion," employing for this purpose a very simple and elegant method. This "mass" is what we have just defined as the transverse mass of the body. We employ the excellent method of these authors in deriving the formula for transverse mass.

Suppose that an experimenter A on the system S_1 constructs a ball B_1 of some rigid elastic material, with unit volume, and puts it in motion with unit velocity in a direction perpendicular to the line of relative motion of S_1 and S_2, the units of measurement employed being those belonging to S_1. Likewise suppose that an experimenter C on S_2 constructs a ball B_2 of the same material, also of unit volume, and puts it in motion with unit velocity in a direction perpendicular to the line of relative motion of S_1 and S_2; we suppose that the measurements made by C are with units belonging to S_2. Assume that the experiment has been so planned that the balls will collide and rebound, over their original paths, the path of each ball being thought of as relative to the system to which it belongs.

Now the relation of the ball B_2 to the system S_1 is the same as that of the ball B_1 to the system S_2, on account of the perfect symmetry which exists between the two systems of reference in accordance with the results of the previous paper (already referred to). Therefore the change of velocity of B_2 relative to its starting point on S_2 as measured by A is equal to the change of velocity of B_1 relative to its starting point on S_1 as measured by C. Now velocity is equal to the ratio of distance to time: and in the direction perpendicular to the line of relative motion of the two systems the units of length are equal; but the units of time are unequal. Hence to either of the observers the change of velocity in the two balls, each with respect to its starting point on its own system, will appear to be unequal.

To A the time unit on S_2 appears to be longer than his own in the ratio $\sqrt{1-\beta^2} : 1$ (see previous paper, theorem IV., p. 167). Hence to A it must appear that the change in velocity of B_2 relative to its starting point is smaller than that of B_1 relative to its starting point in the ratio $\sqrt{1-\beta^2} : 1$. But the change in velocity of each ball multiplied by its mass gives its change in momentum. From postulate C_1 it follows

[1] Phil. Mag., 18 (1909), 510–523. See especially pp. 517–518.

that these two changes of momentum are equal. Hence to A it appears that the mass of the ball B_1 is smaller than that of the ball B_2 in the ratio $\sqrt{1-\beta^2} : 1$.

Similarly, it may be shown that to C it appears that the mass of the ball B_2 is smaller than that of B_1 in the ratio $\sqrt{1-\beta^2} : 1$.

From the general theorems concerning the measurement of length (in the theory of relativity) it follows that if the ball which has been constructed by A were transferred to C's system it would be impossible for C to distinguish A's ball from his own by any considerations of shape and size. Likewise, as A looks at them from his own system he is similarly unable to distinguish them. It is therefore natural to take the mass of C's ball as that which A's would have if it had the velocity v with respect to S_1 of the system S_2. Thus we obtain a relation existing between the mass of a body in motion and at rest.

Now, "mass" as we have measured it above is the transverse mass of our definition. From the argument just carried out we are forced to conclude that the transverse mass of a body in motion depends (in a certain definite way) on the velocity of that motion. The result may be formulated as follows:

THEOREM I. *Let m_0 denote the mass of a body when at rest relative to a system of reference S. When it is moving with a velocity v relative to S denote by $t(m_v)$ its transverse mass, that is, its mass in a direction perpendicular to its line of motion. Then we have*

$$t(m_v) = \frac{m_0}{\sqrt{1-\beta^2}},$$

where $\beta = v/c$ and c is the velocity of light ($MVLRC_1$).[1]

In the statement of this theorem we have tacitly assumed that the mass of a body at rest relative to S, when measured by means of units belonging to S, is independent of the direction in which it is measured. If this assumption were not true we should have a means of detecting the motion of S, a conclusion which is in contradiction to postulate M.

In order to find the longitudinal mass of a moving body we first find the relation which exists between longitudinal mass and transverse mass. We employ for this purpose the elegant method of Bumstead.[2]

Let us as usual consider two systems of reference S_1 and S_2 moving with a relative velocity v, observers A and B being stationed on S_1 and S_2 respectively. Suppose that B performs the following experiment:

[1] These letters attached to the theorem indicate that in its proof we have employed postulates M, V, L, R, C_1. Compare a similar usage in my previous paper.

[2] American Journal of Science (4) 26 (1908), pp. 498–500.

He takes a rod of two units length, whose mass is so small as to be negligible, and attaches to its ends two balls of equal mass. Then he suspends this rod by a wire so as to form a torsion pendulum. We assume that the line of relative motion of the two systems is perpendicular to the line of this wire.

Let us consider the period of this torsion pendulum in the two cases when the rod is clamped to the wire so as to be in equilibrium in each of the following two positions: (1) With its length perpendicular to the line of relative motion of S_1 and S_2; (2) with its length parallel to this line of motion.

As B observes it the period must be the same in the two cases; for, otherwise, he would have a means of detecting his motion by observations made on his system alone, contrary to postulate M. Then from the relation of time units on S_1 and S_2 it follows that the two periods will also appear the same to A. As observed by B the apparent mass of the balls is the same in both cases. We inquire as to how they appear to A. Let m_1 and m_2 be the apparent masses, as observed by A, in the first and second cases respectively. It is obvious that m_1 is the longitudinal mass and m_2 the transverse mass of the balls in question.

When the pendulum is in motion it appears to B that each ball traces a circular arc. From the relations between units of length in the two systems it follows that to A it appears that the balls trace arcs of an ellipse whose semi-axes are 1 and $\sqrt{1-\beta^2}$ and lie perpendicular and parallel, respectively, to the line of relative motion of the two systems.

Let us now determine the period of each of these two pendulums as they are observed by A. By equating the expressions for these periods we shall find the relation which exists between m_1 and m_2.

Let x and y be the cartesian coördinates of a point as determined by A, the axes of reference being the major and minor axes of the ellipse in which the balls move. Let x' and y' be the coördinates of the same point as determined by B. Then the circular path of motion, as determined by B, has the equations

$$x' = \cos\theta, \quad y' = \sin\theta,$$

the angle θ being measured from the major axis of the ellipse. The equations of the ellipse, as determined by A, are

$$x = \cos\theta, \quad y = \sqrt{1-\beta^2}\sin\theta.$$

In the first case—when the rod is perpendicular to the line of relative motion of S_1 and S_2—the amount of twisting in the wire when the ball is in a given position is the absolute value of the corresponding angle θ;

and therefore the potential energy[1] is proportional to θ^2, say that it is $\frac{1}{2}k\theta^2$. Now from the values of y and x above we have

$$y = x\sqrt{1 - \beta^2}\tan\theta.$$

For small oscillations we have $x = 1$ and $\tan\theta = \theta$; and therefore

$$y = \sqrt{1 - \beta^2}\cdot\theta.$$

Hence the potential energy is

$$\frac{1}{2}\frac{k}{1 - \beta^2}y^2;$$

and the equation of motion of the particle becomes

$$m_1\frac{d^2y}{dt^2} = -\frac{k}{1 - \beta^2}y.$$

Hence the period T_1 of oscillation is

$$T_1 = 2\pi\sqrt{\frac{m_1(1 - \beta^2)}{k}}.$$

In the second case—when the rod is parallel to the line of relative motion of S_1 and S_2—the amount of twisting in the wire for a given position of the balls is the absolute value of $(\pi/2) - \theta$. The potential energy is $\frac{1}{2}k[(\pi/2) - \theta]^2$. We have

$$x = \frac{y}{\sqrt{1 - \beta^2}}\cot\theta.$$

For small oscillations we have

$$y = \sqrt{1 - \beta^2},\ \cot\theta = \tan\left(\frac{\pi}{2} - \theta\right) = \frac{\pi}{2} - \theta.$$

Hence the potential energy is $\frac{1}{2}kx^2$, and the period T_2 of oscillation is therefore

$$T_2 = 2\pi\sqrt{\frac{m_2}{k}}.$$

Equating the two periods of oscillation found above we have

$$m_2 = (1 - \beta^2)m_1.$$

[1] That the potential energy is proportional to θ^2 when measured by B is obvious. Since A observes a different apparent angle θ' (say) corresponding to B's observed angle θ it might at first sight appear that the potential energy as observed by A is proportional to θ'^2. That this is not the case is seen from the fact that for a given twist in the wire θ' depends on the direction of equilibrium of the bar, that is, it depends on the way in which the bar is attached to the wire; hence, if the potential energy as observed by A were proportional to θ'^2 it would depend on the way in which the bar is attached. Since this is obviously not the case we conclude that the potential energy is proportional to θ^2.

Remembering that m_1 and m_2 are the longitudinal mass and transverse mass, respectively, and making use of theorem I., we have the following result:

THEOREM II. *Let m_0 denote the mass of a body when at rest relative to a system of reference S. When it is moving with a velocity v relative to S denote by $l(m_v)$ its longitudinal mass, that is, its mass in a direction parallel to its line of motion. Then we have*

$$l(m_v) = \frac{m_0}{(1 - \beta^2)^{\frac{3}{2}}},$$

where $\beta = v/c$ and c is the velocity of light ($MVLRC_1C_2$).

§ 3. ON THE DIMENSIONS OF UNITS.

Denote the fundamental measurable physical entities mass, length and time by M, L and T respectively. Then the definition of derived entities gives rise to the so-called dimensional equations. Thus if B denote velocity, then from the definition of velocity we have the dimensional equation

$$V = \frac{L}{T}.$$

That such equations must be useful in obtaining the relations of a derived unit in two systems of reference is obvious. Thus from the above dimensional equation for V we may at once derive the fundamental result (see previous paper, theorem VI., p. 170) concerning the relation of units of length in the line of relative motion of two systems not at rest relatively to each other. For this purpose it is sufficient to employ postulate V. and theorem IV. of the previous paper. The reader can easily supply the argument. Or, conversely, if one knows the relations which exist between units of length and units of time in two systems one concludes readily to the truth of postulate V.

Likewise, from the dimensional equation

$$\text{acceleration} = \frac{L}{T^2}$$

one may readily determine the relations which exist between units of acceleration on two systems, it being assumed that the relations of time units and length units are known. Making this assumption, then, the two dimensional equations above give us the following theorem:

THEOREM III. *Let two systems S_1 and S_2 move with a relative velocity v in the direction of a line l, and let $\beta = v/c$ where c is the velocity of light. Then to an observer on S_1 it appears that the unit of velocity [acceleration] on*

S_1 bears to the unit of velocity [acceleration] on S_2 the ratio $1 : 1$ $[1 : \sqrt{1-\beta^2}]$ *or* $1 : \sqrt{1-\beta^2}$ $[1 : 1-\beta^2]$ *according as the motion is parallel to l or perpendicular to l ($MVLR$).*

Let us use F to denote force. Then from the dimensional equation

$$F = \frac{ML}{T^2},$$

we shall be able to draw an interesting conclusion concerning the measurement of force.

Suppose that an observer B on a system S_2 carries out some observations concerning a certain rectilinear motion, measuring the quantities M', L', T', so that he has the equation

$$F' = \frac{M'L'}{T'^2}.$$

Another observer A on a system S_1 (having with respect to S_2 the velocity v in the line l) measures the same force, calling it F. Required the value of F in terms of F', when the motion is parallel to l and when it is perpendicular to l, the estimate being made by A.

When the motion is perpendicular to l—that is, when the force acts in a line perpendicular to l—we have

$$F_1 = \frac{ML}{T^2} = \frac{M'\sqrt{1-\beta^2}\cdot L'}{T'^2(1-\beta^2)} = \frac{F'}{\sqrt{1-\beta^2}}.$$

When the motion is parallel to l we have

$$F_2 = \frac{ML}{T^2} = \frac{M'(1-\beta^2)^{\frac{3}{2}}\cdot L'\sqrt{1-\beta^2}}{T'^2(1-\beta^2)} = (1-\beta^2)F'.$$

These results may be stated in the following theorem:

THEOREM IV. *In the same systems of reference as in theorem III., let an observer on S_2 measure a given force F' in a direction perpendicular to l and in a direction parallel to l, and let F_1 and F_2 be the values of this force as measured in the first and second cases respectively by an observer on S_1. Then we have*

$$F_1 = \frac{F'}{\sqrt{1-\beta^2}}, \quad F_2 = (1-\beta^2)F' \qquad (MVLRC_1C_2).$$

It is obvious that a similar use may be made of the dimensional equation of any derived unit in determining the relation which exists between this unit in two relatively moving systems of reference.

§ 4. EQUIVALENTS OF THE POSTULATES.

The problem of determining sets of postulates logically equivalent to those which have been used as a basis of the theory of relativity is obviously important. So far as a justification of the theory is concerned it is, however, unnecessary to have complete logical equivalents; all that is essential is to find a set of postulates, experimentally demonstrable, by means of which it is possible to demonstrate the characteristic conclusions of relativity concerning the relations of units of time and units of length in two systems of reference.[1] Such a set of postulates we shall call *essential equivalents* of the postulates of relativity. The object of this section is to determine essential equivalents of postulate R, that is, such postulates as may be taken in connection with postulates M, V, L, so that the new set shall be essentially equivalent to M, V, L, R.

For this purpose let us first consider the relation between the transverse mass of a moving body and its mass at rest as given in theorem I. Let us suppose that this theorem is true[2] (whether proved experimentally or otherwise); and let us seek its consequences. Suppose that the experiment by means of which we proved theorem I. is now repeated. If we again assume the law of conservation of momentum and equate the two observed changes in momenta, it is clear that we shall have a relation between measurements of time as carried out in the two systems of reference, and that this relation will be precisely the same as in the usual theory of relativity. Having this relation concerning time units we can then proceed as in the first paragraph in § 3 to derive the usual relations between units of length. Hence we have the following result:

THEOREM V. *If m_0 and $t(m_v)$ have the same meaning as in theorem I. and if for any particular kind of matter whatever we have the relation*

$$t(m_v) = \frac{m_0}{\sqrt{1 - \beta^2}},$$

then this fact and postulates ($MVLC_1$) form an essential equivalent of postulates ($MVLRC_1$).

Next, let us suppose that for some particular kind of matter we have the relation

$$t(m_v) = (1 - \beta^2) l(m_v),$$

where $t(m_v)$ and $l(m_v)$ denote the transverse mass and the longitudinal mass, respectively, as above. Then repeat the experiments by means of

[1] It is obvious that we should then be able to demonstrate theorems I. and II. concerning the mass of a moving body.

[2] All that is essential to the argument is the truth of theorem I. for a particle of matter of some one kind; it need not be assumed to be true universally.

which we proved theorem II. As before the balls will appear to B to move on arcs of the circle

$$x' = \cos\theta, \quad y' = \sin\theta.$$

Suppose that to A they appear to move along arcs of the ellipse[1]

$$x = \cos\theta, \quad y = \rho\sin\theta,$$

where ρ is a constant to be determined. As before, without the use of postulate R, it may be shown that to A the periods will be the same in the two cases. Then determine the periods as in the preceding discussion. The expressions for the period will contain ρ; in fact on equating them we shall find

$$m_2 = \rho^2 m_1.$$

But $m_1 = l(m_v)$ and $m_2 = t(m_v)$ whence on account of the relations between $l(m_v)$ and $t(m_v)$, we have at once

$$\rho = \sqrt{1 - \beta^2}.$$

This, in connection with postulate L, leads readily to the usual relations concerning the units of length in two systems of reference. Having these relations of length units, the dimensional equation

$$V = \frac{L}{T}$$

taken in connection with postulate V leads at once to the usual relation of time units, provided we take the motion along the line of relative motion of the two systems. Hence we have the following theorem:

THEOREM VI. *If $l(m_v)$ and $t(m_v)$ have the same meaning as in theorems I. and II. and if for any particular kind of matter whatever we have the relation*

$$t(m_v) = (1 - \beta^2)\cdot l(m_v),$$

then this fact and postulates $(MVLC_1C_2)$ are essential equivalents of postulates $(MVLRC_1C_2)$.

§ 5. THE BUCHERER EXPERIMENT.[2]

Our postulates V, L, C_1 have been universally accepted as part of the basis of the classical mechanics. Many persons have found no difficulty in accepting postulate M; certain it is at least that we have absolutely no evidence to contradict it. We have seen in theorem V. that these four postulates, taken in connection with the formula for transverse mass, form

[1] Since we are assuming postulate L it is clear that the path must be of this form.

[2] Compare Tolman, PHYSICAL REVIEW, 31 (1910), p. 36.

an essential equivalent of $(MVLRC_1)$; in other words, the experimental demonstration of the formula for transverse mass carries with it the experimental proof of the theory of relativity, provided that postulates $(MVLC_1)$ are accepted as experimentally proved.

Bucherer[1] has carried out some investigations which have been supposed to furnish this experimental verification for the formula of transverse mass, and hence for the whole theory of relativity. In order to draw this conclusion from Bucherer's direct results it is necessary to make use of a law which we have not yet employed, namely, the law of conservation of electricity which we have stated as postulate C_3. Since this law has customarily been accepted and has not yet led to contradictions it should certainly still be supposed to hold. Accepting it, then, we have in Bucherer's results a partial experimental confirmation of the theory of relativity, as we now show.

Bucherer's investigations have to do with the mass of a moving electron. There seems to be no means at hand for a direct measurement of this mass, and Bucherer resorted to the expedient of determining the ratio of charge to mass. Let us denote the charge by e, which we suppose to be constant, in accordance with postulate C_3. As before let m_0 and $t(m_v)$ denote the mass at rest and the mass when moving with velocity v, of the electron in consideration. Bucherer's experiments were carried out to determine the relation which exists between e/m_0 and $e/t(m_v)$. The measurements agreed in a remarkable way, not only as to general characteristics but also as to exact numerical results, with the formula[2]

$$\frac{e}{t(m_v)} = \frac{e\sqrt{1-\beta^2}}{m^0}.$$

Taking this formula as thus experimentally demonstrated we have at once our fundamental relation for transverse mass: $\sqrt{1-\beta^2}\,t(m_v) = m_0$.

From this it follows that the experimental demonstration of the theory of relativity is complete when we have proved M, V, L, C_1 and C_3, provided that one accepts Bucherer's proof of the above relation between e/m_0 and $e/t(m_v)$. That is, *the essentials of the theory of relativity flow from*

[1] Annalen der Physik (4) 28 (1909), 513–536.

[2] As a matter of fact Bucherer did not measure the ratio e/m_0. Instead of this he considered the ratio $e/t(m_v)$ for a considerable range of values of v and noticed that its value always agreed with the formula $e/t(m_v) = k\sqrt{1-\beta^2}$, where k is a constant. It appears natural, then, to assume that $m_0 = e/k$, whence one has the formula in the text. It should be emphasized that this assumption is necessary in order that the Bucherer results may be associated with our theorem as in the text, and consequently the conclusions there reached can be accepted with no stronger confidence than that which one has in the accuracy of the above assumption. See the next section where a means of experimental verification of the theory of relativity is suggested which does not depend on this assumption for its validity.

principles for each of which there is strong experimental confirmation. This important conclusion has often been pointed out.

To the present writer, however, it seems that one point especially should be subjected to further examination. Is it in fact true that the charge of a moving electron is independent of the velocity with which it moves? Let e_0 be the charge of the electron when at rest and denote by $t(e_v)$ its apparent charge when in motion with velocity v, the charge being measured by means of tests in which the line of action is perpendicular to the line of motion of the charge. In the above work we have assumed, in accordance with the usual practice, that $e_0 = t(e_v)$. Suppose however that the true relation were different from this, that, in fact, we have

$$t(e_v) = e_0\sqrt{1 - \beta^2};$$

then Bucherer's experiment would lead to the conclusion that $t(m_v) = m_0$, and thus the whole theory of relativity would be overturned. Furthermore, if any relation other than $e_0 = t(e_v)$ is the true one, some modification at least of the theory of relativity would have to be made or else one would have to give up postulate C_1 which asserts the law of conservation of momentum. This result brings to notice the great importance of the question of the constancy of electric charge on the electron. We shall treat this matter further in the next section.

§ 6. Another Means for the Experimental Verification of the Theory of Relativity.

Just as theorem V. was used for the theoretical basis of Bucherer's (partial) experimental demonstration of the theory of relativity so theorem VI. may be employed as the theoretical basis of a new experimental investigation which has not yet been carried out, one which bears the same essential relation as that of Bucherer to the confirmation or disproof of the entire theory of relativity. The object of this section is to indicate the nature of this experiment.

Let e_0 denote the charge of an electron when at rest with respect to a given system of reference. When it is in motion with a velocity v let $t(e_v)$ and $l(e_v)$ be the apparent charge when measured by means of tests whose lines of action are perpendicular and parallel, respectively, to the line of motion of the electron.

If we employ postulate C_3 we conclude that $e_0 = t(e_v) = l(e_v)$. We shall first assume the truth of one of these relations, namely, $t(e_v) = l(e_v)$, and we shall denote the common value of these two quantities by e. Now let us suppose that some means are found for measuring both the

quantities $e/t(m_v)$ and $e/l(m_v)$, where $t(m_v)$ and $l(m_v)$ denote as usual the transverse mass and the longitudinal mass respectively of the moving electron, whose velocity is v. Bucherer's methods furnish the means of measuring the first of these ratios; it will be necessary to devise a way to determine the value of the second ratio.

Or, instead of finding a means of measuring the two quantities $e/t(m_v)$ and $e/l(m_v)$ it will be sufficient if one determines only their ratio, as will be obvious from the discussion following.

Suppose now that we find the relation predicted by the theory of relativity:

$$\frac{e}{t(m_v)} = \frac{e}{(1 - \beta^2)l(m_v)}.$$

This equation leads to the relation $t(m_v) = (1 - \beta^2) \cdot l(m_v)$. According to theorem VI. this would give a new experimental confirmation of the theory of relativity. The importance of such a result is apparent.

But we should also have more than this. Having now concluded that the theory of relativity is confirmed and this result having been reached without the use of a relation between e_0 and $t(e_v)$ we may now use the experiment of Bucherer to draw further conclusions concerning electric charges in motion. In particular, it is obvious that we should have a proof of the fundamental relation

$$e_0 = t(e_v).$$

That is to say, having assumed that $t(e_v)$ and $l(e_v)$ are equal we conclude further on experimental evidence that each of these is equal to e_0. Now it is difficult to conceive how $t(e_v)$ and $l(e_v)$ could be different, for this would imply that the notion of electric charge is in need of essential modification. In fact, if the charged body is moving, the notion of charge would be indefinite in meaning until we had assigned the direction along which such charge is to be measured. Thus, if the experiment should turn out as surmised above, we should not only have the strongest sort of experimental confirmation of the theory of relativity but we should also have a valuable verification of the fact that an electric charge does not vary in amount with the velocity of the body which carries it.

Suppose, on the other hand, that we make no assumption concerning the relation of $t(e_v)$ and $l(e_v)$ or of $t(m_v)$ and $l(m_v)$. On carrying out the experiments a relation of the form

$$\frac{t(e_v)}{t(m_v)} = k \frac{l(e_v)}{l(m_v)}$$

will be obtained where k is a constant or a variable depending on v. If

it is found that k is different from unity we shall be forced to the conclusion that either our conception of mass in the classical mechanics or our conception of charge in the classical electrical theory is in need of essential modification. Again, if $k = 1$ and if we assume, as is natural, that $t(e_v) = l(e_v)$ then we have an experimental disproof of the theory of relativity. In fact we have such a disproof unless $k = 1/(1 - \beta^2)$, provided of course that we assume $t(e_v) = l(e_v)$.

From these remarks it is obvious that, whatever may be the result of the experiments, they will certainly lead to important conclusions of a fundamental nature; that is, we have here a *crucial* experiment, one that cannot fail to lead somewhither. It is to be hoped that some laboratory worker will soon perform the requisite experiments; the writer, who is a mathematician, can only regret that he cannot conveniently carry out the work himself.

A variation of the experiment of Bucherer would seem to be sufficient for the purpose here. Bucherer's results were obtained by subjecting the moving electron to a magnetic field and also to an electric field each at right angles to the line of motion. A variation of the direction of these fields relative to the line of motion of the electron would probably afford a means of making the necessary measurements for the experimental proof of the relations requisite for use in the preceding discussion.

§ 7. Mass and Energy.

If, as is frequently done, we employ for the definition of the kinetic energy E the relation (compare § 1)

$$E = \int_0^v M dv = \int_0^v mv dv,$$

it is clear that for the mass m we should take the longitudinal mass $l(m_v)$. Then let m_0 denote the mass of the body at rest, E_0 its energy when at rest (that is, the energy due to its internal activity), and E_v its energy when moving at the velocity v. Then clearly $E = E_v - E_0$, so that in view of theorem II. we have

$$E = E_v - E_0 = \int_0^v \frac{m_0 v dv}{(1 - \beta^2)^{\frac{3}{2}}};$$

whence, on integration, we have

$$E = E_v - E_0 = m_0 c^2 \left(\frac{1}{\sqrt{1 - \beta^2}} - 1 \right). \tag{1}$$

Hence for the kinetic energy of a moving body we have

$$E = m_0 c^2 (\tfrac{1}{2}\beta^2 + \tfrac{3}{8}\beta^4 + \cdots);$$

or, to a first approximation only,

$$E = \tfrac{1}{2}m_0v^2.$$

Therefore the usual formula for kinetic energy in the classical mechanics is only a first approximation.

Since relation (1) is to be true for all velocities v it is obvious that we have

$$E_v = \frac{m_0c^2}{\sqrt{1-\beta^2}} + k, \quad E_0 = m_0c^2 + k,$$

where k is a constant, that is, a quantity independent of v. From the first of these equations we conclude further that

$$E_v = c^2 \cdot t(m_v) + k,$$

so that the total energy of a body, decreased by the constant k, is directly proportional to its transverse mass. In case the body is at rest its mass in one direction is the same as in another; hence $m_0 = t(m_0)$. Bearing this in mind we have the following theorem:

THEOREM VII. *Let m_0 be the mass of a body when at rest with respect to a given system of reference and let $t(m_v)$ denote its transverse mass when it is moving with the velocity v (the case $v = 0$ is not excluded). Then the total energy E_v which it possesses is $c^2t(m_v) + k$, where k is a constant.*

The following relations are immediate consequences of equations written out above:

$$\frac{E_v - E_0}{t(m_v) - m_0} = c^2, \quad E_v - k = \frac{E_0 - k}{\sqrt{1-\beta^2}}.$$

Now, suppose that an experimenter contributes to a body which is at rest a known amount of energy and determines the velocity which this causes the body to acquire. If the two measurements are made with sufficient accuracy one will be able, by substituting the results in the first of the above equations, to determine in this way the velocity of light. Actually to carry out this remarkable method for measuring c would doubtless be very difficult; but the obvious great importance of the result is certainly such as to justify a careful consideration of the problem. If the value of c determined in this way should agree well with its value as otherwise found, this would give us an interesting confirmation of the theory of relativity.

Let us consider the mass of a rotating top, the mass being measured along the axis of rotation. According to our results this mass should be different from that of the same top when at rest, and the difference should bear a definite relation to the amount of energy which is involved

in the rotation. If the measurements here involved could be made with sufficient accuracy we would have another means, independent of light itself, for the measurement of the light-velocity c. Again, this experiment would afford us a measure of transverse mass and in that way could lead to a confirmation of the theory of relativity, provided that we assume c as known from independent measurements; and this confirmation, it is to be noticed, would be independent of electrical considerations.

It seems to be impossible to determine the constant k which enters into the above discussion. But in the absence of any evidence to the contrary it would appear natural tentatively to assume that k is zero. On the basis of this assumption we should have the following remarkable conclusions: The mass of a body at rest is simply the measure of its internal energy. The transverse mass of a body in motion is the measure of its internal energy and its kinetic energy taken together.[1] Its longitudinal mass is its total energy multiplied by a simple factor. (The longitudinal mass, therefore, bears a simple ratio to the total energy.) One can hardly resist the conclusion that the transverse mass of a body depends entirely on its energy, and therefore that matter is merely one manifestation of energy.

§ 8. Remarks on the Principle of Least Action.

In the preceding section we have seen that in the theory of relativity the classical formula $E = \frac{1}{2}mv^2$ for the measure of kinetic energy is true only as a first approximation. This is due to the fact that mass is a variable quantity. But the conclusion does not appear to necessitate our surrender of the law of conservation of energy.

The same causes which lead to a modification in the formula for E will also require a corresponding modification in the value of the action A as defined in § 1. The question arises as to whether the principle of least action is left intact. I cannot enter upon the investigation here; but the problem seems to me to be of importance, and consequently I am stating it in the hope that some one will be led to consider its solution.

Undoubtedly the principle of least action is one which should be given up only when there are strong reasons for it. It is a mathematical formulation of the law that nature accomplishes her ends with the least possible expenditure of labor, so to speak. Certainly this law is one which appeals to our minds with strong force. There is something about it which is æsthetically satisfying in a high degree. It seems to me, however, that a fresh study of it should be made in the light of the theory of relativity.

[1] Compare Lewis and Tolman, Phil. Mag. (6) 18 (1909), p. 521.

§ 9. SPECULATIVE CONSIDERATIONS.

From some results in the preceding discussion it has appeared that the transverse mass of a body is merely a manifestation of its total energy, that it is in fact a measure of that energy. It is then natural to suppose, on the other hand, that anything which possesses energy has mass; and we thus conceive of mass and energy as coextensive.

Now a beam of light possesses energy; whence we conclude naturally that it also has mass. But we have seen that no "material body" can have a velocity as great as that of light. How are these two facts to be reconciled? If we define "matter" as that which possesses mass (and this is probably the best definition) we shall perhaps best be able to represent to ourselves the nature of matter if we think of it as a strain in the ether. Then the two facts which we have to reconcile would be entirely consistent if we suppose that the beam of light sets up a strain in the ether (whence its mass) but that this strain as a whole is not propagated with the velocity of light. In fact, if it moves at all it is probably with a velocity relatively much smaller than that of light.

Again, if mass is merely a manifestation of energy in the form of a strain in the ether it would follow that gravitation is simply an interaction among these several strains. A strain principally localized in one place would have lines of strain going out from it in all directions, and the action of these lines of strain upon one another would afford the effective means by which gravitation acts.

Whether these strains should be thought of as static in the ether or as due to the relative motion of the parts of the ether would probably be determined differently by different minds. If one inclines to the latter form of representation, the necessary movement might be conceived of as vortex whorls in the ether, setting up strains and lines of strain by aid of which we are able to interpret observed phenomena.

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